EPA-903-R-99-024

Chesapeake Bay Program Mainstem Coordinated Split Sample Program Report 1994-1998

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I. INTRODUCTION

The Monitoring Subcommittee of the Chesapeake Bay Program initiated the Chesapeake Bay Coordinated Split Sample Program (CSSP) in 1988. It's goal is to assess the comparability of water quality results from the 9 analytical laboratories that participate in the Chesapeake Bay Monitoring Program. This goal is achieved by identifying any parameters that have low inter-laboratory agreement and by estimating the measurement system variability.

Identifying parameters with low agreement enables the labs and organizations involved to investigate significant differences among their methods, and take actions to raise their inter-laboratory agreement. This might involve changing field methods, laboratory methods, or both. It is important to note that the split sample variability can come from variability in field sampling as well as lab analysis variability. Therefore, laboratory variability includes all elements of the measurement system: field sampling, sample handling, lab analysis, data handling and the state or municipal agency that supervise the water quality monitoring program.

Estimates of the variability of the measurement system are useful to data users such as statisticians and modelers who need confidence bounds for monitoring data. Although split sample results do not include routine sampling variability, they are the best measurements we have available to estimate variability of the total system of Chesapeake Bay water quality monitoring data.

The CSSP has three components, each including three to five labs that analyze samples from similar salinity regimes and concentration ranges (CBP 1991). Labs from each component analyze triplicate field samples that are collected quarterly with the exception of the Fall Line component, which is sampled twice a year due to budgetary constraints. Labs send the analytical results to the EPA Chesapeake Bay Program Office (CBPO) in Annapolis for data analysis.

This report summarizes the 1994-1998 results from the mainstem component of the Coordinated Split Sample Program. The mainstem component is the only component that analyzes saline water samples. This component includes two mainstem labs: Chesapeake Biological Laboratory (CBL) and Old Dominion University (ODU). It also includes a Maryland tributary lab, Maryland Department of Health and Mental Hygiene (MDHMH), and a Virginia tributary lab, Division of Consolidated Laboratory Services (DCLS). The split samples are collected by the Maryland Department of Natural Resources. (Figure 1)

Mainstem Split

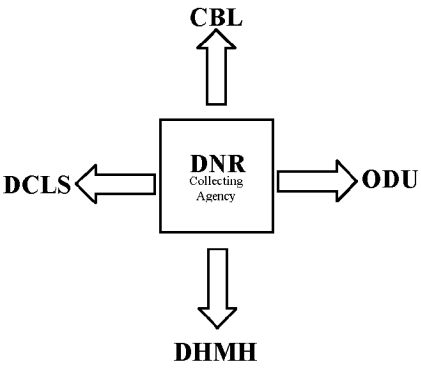


Figure 1

II. METHODS

A. SAMPLE COLLECTION AND SPLITTING

A field crew from the Maryland Department of Natural Resources (MD DNR) collected quarterly split samples from the surface layer at station MCB4.4. The field crew followed the splitting procedures in the CSSP Guidelines (CBP 1991). One large sample is stirred on the boat in a 15 gallon carboy with stirring rod connected to an electric drill. Subsamples were drawn sequentially from a spigot at the bottom of the carboy into 1 liter polyethylene bottles. The bottles from subsample 1 are dispensed in the sequence MDHMH- CBL-ODU-DCLS, followed by the bottles for subsamples 2 and 3.

B. ANALYTICAL CHEMISTRY METHODS

Historically, the mainstem labs use different analytical methods than the two tributary labs. Mainstem labs measure the dissolved and particulate fractions, while the tributary labs measure the total and the dissolved fractions and then calculate the particulate fractions. However, in 1995 DCLS began measuring the dissolved and particulate fractions. All laboratories filter their samples between 8 and 10 am the day after collection. Methods are discussed in greater detail within the sections describing the results for each parameter.

C. DATA ANALYSIS AND GRAPHING

Inter-laboratory agreement is the tendency for split sample results from different labs and organizations to be consistently similar over time. Any pairs of labs that have a large and recurring inter-laboratory difference are said to have low agreement. A decision rule was developed to identify which parameters had inter-laboratory differences that were large and consistent enough to warrant investigation by the organizations involved. Based upon discussions by the Analytical Methods and Quality Assurance Workgroup (AMQAW) on 4/24/90 and 1/26/93, the decision was based on graphs of the data with precision bars, and the results of appropriate statistical tests. Graphs with precision bars will show the magnitude of the differences for any one given sample date, while the statistical test is more sensitive to the consistency of the differences over time. Further investigation was recommended if:

1) more than half of the sampling dates had pairwise inter-laboratory diffferences that were larger than within organization precision, (if the error bars don't overlap), **and**,

2) an appropriate statistical test had a probability (p) ≤ 0.01 that the differences between labs was due to chance alone and not analytical differences.

Parameters identified by this combination of factors usually have different field and/or laboratory methods at one or more of the laboratories involved.

Graphs of the split sample results show which labs had results that were farther apart than their own laboratory precision estimates. The within-laboratory precision estimates for CSSP analysis were either 1) the standard error of the three subsamples for each sample date; or 2) 2x the standard error of the difference between the calculated and observed value the lab obtains when analyzing standard reference material (SRM) for the variable in question. No labs analyzed SRMs for every parameter. See Table 1 for a description of what value was used (standard error of the three replicates or a combination of the standard error of the three replicates and the standard error of the SRM data) in determining the error bars. Graphs of the means for each sample date for each lab were drawn showing this within-laboratory precision as "error bars". Any pairs of lab means that do not have overlapping "error bars" have differences that were larger than their within-laboratory precision.

A multi-factor ANOVA was used to assess interlaboratory agreement using the CSSP split sample data. Factors examined in the data were **date**, **replicate number**, **lab** and **date/lab** interaction. Due to the assumptions of the ANOVA, if a lab was missing all data for a particular date, that date was dropped from the analysis. If the results of the ANOVA suggested that there was significant interlab variability (i.e. a significant difference among labs, $p < 0.01$), then the data were subjected to a Least Squares Means analysis. The **replicate** factor of the ANOVA examined the data for differences associated with replicate number (1, 2 or 3). A significant difference, as determined by the **replicate** factor, could be an indication of inefficient mixing of the reservoir from which the replicates are split. The **lab** factor examined the data for variance associated with a lab and the **date/lab** factor determined if variability associated with the labs was variable over time. The ANOVA was then rerun with the **lab factor** using the **date/lab** mean square error term. This was done to determine if the difference among labs was greater than the within run variability associated with each lab.

In the Least Squares Means analysis, the mean concentration for each lab was compared to the mean concentration of the other labs (for the mainstem – 4 labs for a total of 6 comparisons). From this, it could be determined which labs were significantly different from one another. A Least Squares Means analysis was also conducted on the mean of the absolute value of the residuals for each lab's split sample data. This analysis gave some insight into the analytical precision of each lab relative to the other labs. The Least Squares Means results are summarized graphically in the parameter sections of this report. An example graphic is displayed in figure 2.

Figure 2. The above diagram summarizes an example Least Squares Means Analysis. Labs are ordered from left to right in terms of increasing variability. Labs underlined by the same line are not significantly different from one another in terms of their variability

Table 1 – Table describing what value was used for the error bars in the graphs of the split sample results. "SRM" indicates that the error bar is 2x the standard error of the difference between the calculated and observed value the lab obtains when analyzing standard reference material (SRM) for the variable in question. "Split" indicates that the error bar is the standard error of the three subsamples for each sample date.

Parameter	CBL	ODU	DCLS	DHMH
TDP	SRM	SRM	SRM	Split
PP	Split	Split	Split	Split
PO4f	SRM	SRM	SRM	SRM
TP	Split	Split	Split	Split
TDN	SRM	SRM	SRM	Split
NH4	SRM	SRM	SRM	SRM
NO23	SRM	SRM	Split	SRM
NO2	Split	Split	Split	Split
TSS	Split	Split	Split	Split
PC	Split	Split	Split	Split
Si	Split	Split	Split	Split
PN	Split	Split	Split	Split

The ANOVA and Graphical analyses were run twice. Once on the entire 1994-1998 data set (20 sampling dates) and once on data from September of 1997 through the end of 1998 (6 sampling dates). The latter was conducted with the intention of detecting recent or developing problems among the labs.

III. Summary of Analytical Results

A) Within Laboratory Precision

Three estimates of within laboratory precision and bias were used in this analysis: the coefficient of variation (CV) of the three field replicates from each split (precision), the percent spike recovery and the standard reference material (SRM) percent recovery (bias). The CV expresses the standard deviation of the three replicates as a percentage of the mean of the three replicates. A lower CV indicates a higher degree of precision. If a lab is consistently obtaining CVs above 25% for a given parameter, further investigation may be required. However, CVs tend to be related to concentration. As concentration decreases, variability increases and the standard deviation becomes a larger percentage of a smaller mean.

The percent spike recovery is determined by spiking an aliquot of one of the three replicates with a known concentration. The measured value is then expressed as a percentage of the expected value. SRM analyses for selected parameters are conducted within the same run as the three split sample replicates for that parameter. SRM percent recoveries are determined by analyzing a sample of known concentration and calculating a percentage based on the measured value and the expected value. Percent recovery values should be between 90 and 110%. Values less than 80% or greater than 120% are indicative of a problem.

Laboratory CVs for each parameter and sampling date were generally low (summarized in the method comparison tables for each parameter; complete data available in Appendix A). There were a few exceptions to this however. DHMH had CVs exceeding 25% for total dissolved phosphorus and particulate phosphorus on six of fourteen dates and twelve of fifteen dates respectively. CBL had CVs exceeding 25% for PO4f and NH4 on seven of sixteen dates and six of sixteen dates respectively. DCLS had CVs exceeding 25% for PC on seven of eight dates.

Spike percent recoveries and SRM percent recoveries were generally good for all labs. All of the mean and median spike percent recoveries for every parameter measured by each lab were well within the 90 to 110% range. also good for all labs. SRM recoveries almost all fell within the 90 to 110% range.

B) Interlaboratory Agreement

Of the twelve parameters analyzed, seven had significant differences between at least two of labs according to both the Least Squares Means analysis and the graphical analysis. These parameters were TDP, PP, TP, TDN, TSS, PC and PN. When the analyses were done on the September 1997 through December 1998 data significant differences between at least two labs were found only for TDP, TSS and PN. These results are summarized in Table 2.

Table 2 – Table summarizes the results of the Least Squares Means analysis of means and residuals and the graphical analysis. Significant indicates that significant differences were found

Parameter	1994 – 1998 LS Means of Means	1994 – 1998 LS Means of Residuals	1994 –1998 Graphical Analysis	1997.5 – 1998 LS Means of Means	1997.5 – 1998 LS Means of Residuals	1997.5 –1998 Graphical Analysis
Total Dissolved Phosphorus	Significant	Significant	Significant	Significant	Not Significant	Significant
Particulate Phosphorus	Significant	Significant	Significant	Not Significant	Significant	Not Significant
Ortho-Phosphate	Significant	Significant	Not Significant	Not Significant	Significant	Significant
Total Phoshorus	Significant	Significant	Significant	Not Significant	Not Significant	Significant
Total Dissolved Nitrogen	Significant	Not Significant	Significant	Not Significant	Not Significant	Significant
Particulate Nitrogen	Significant	Not Significant	Significant	Significant	Not Significant	Significant
Ammonium	Not Significant	Not Significant	Not Significant	Not Significant	Not Significant	Significant
Nitrate + Nitrite	Not Significant	Not Significant	Significant	Not Significant	Not Significant	Not Significant
Nitrite	Not Significant	Not Significant	Significant	Not Significant	Not Significant	Significant
Total Suspended Solids	Significant	Not Significant	Significant	Significant	Not Significant	Significant
Particulate Carbon	Significant	Not Significant	Significant	Not Significant	Not Significant	Significant
Silica	Not Significant	Not Significant	Significant	Not Significant	Not Significant	Significant
Chlorophyll-a	NA	NA	NA	NA	NA	NA

Mainstem Split Results
By Parameter

Parameter: Total Dissolved Phosphorus

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Total Dissolved Phosphorus Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F 30 ml glass test tube	Vacuum, 0.7μm GF/F HDPE, 250 ml	Vacuum, 0.7μm GF/F HDPE	Vacuum,0.7μm GF/F HDPE
Glassware	Graduated cylinders. Glass tubes cleaned w/ 10% HCl, DI rinsed, autoclaved with potassium persulfate before use.	Class A volumetric. Dedicated glass tubes. *1/94-5/97*: Dichromic acid soak w/ RGW rinse. *After 6/97*: Liquinox , w/tap water rinse, rinsed twice w/ 4N HCl then 9X w/RGW.	Rainin auto pipet. Digestion tubes autoclaved with persulfate before use. Dedicated glassware washed in 1:1 HCl, DI rinsed.	Disposable 30 ml borosilicate tubes w/ polypropylene screw caps
Method	Alkaline persulfate digestion (60 min @ 4psi) + EPA 365.1- automated ascorbic acid method. (Valderrama, 1981 & D Elia et.al, 1977)	*1/94-5/97*: EPA 365.3 Manual ascorbic acid by std. addition) *6/97 on*: Alkaline persulfate digestion (autoclave 30min@ 105 ec) + EPA 365.1 - auto. ascorbic acid method.	Alkaline persulfate digestion + EPA 365.1- automated ascorbic acid method.	EPA 365.4: Acid block digestion (H_2SO_4, K_2SO_4 & $HgSO_4$) + automated ascorbic acid method.
Instrumentation	Technicon AAII; 880 nm 37 °C heat bath, 50 mm flow cell	*1/94-5/97*: Perkin Elmer λ-1 single beam spec. *6/97 on*: Skalar SAN^{plus}, 880 nm. Auto background/ matrix correct (1010nm), 75 mm flow cell, 40°C heat bath	Skalar SAN^{plus}, 880nm. Auto background/ matrix correction w/ 1010nm filter. 50 mm flow cell	Alpkem model 3570 with SoftPac software 660 nm heat bath.
Inst. Maintenance	Rinsed w 1N HCl for 15 min. after analysis, DI for 15 min.	Rinsed w/ RGW for 30 min. after analysis. Weekly: Cartridge cleaned w 0.5 N NaOH for hr. and RGW for hour. Align flowcell.	Rinsed w/ DI water daily. Rinsed w/ 0.5 N NaOH for hr. weekly	Rinse w/DI for 15 min, 15 min w/10% HCL, 20 min with DI, 30 min with 1N NaOH, 30 min w/DI water.

Reagents	Potassium persulfate, boric acid for digestion. Two reagents, DI, SDS wetting agent for analysis	1/94-5/97: Two reagents, 6/97 on: Combined reagent, RGW, FFD-6 wetting agent.	Two reagents, FFD-6 wetting agent	Two reagents, NaCl diluent, Dowfax 2A1 wetting agent
Standards & blanks	KH_2PO_4 in DI H_2O 3 standards & DI blanks are digested. Glycerophosphate internal (check) standard.	*1/94-5/97*: KH_2PO_4 in com-posite of filter. sample water. *6/97 on*: Artificial sea water (ASW) salinity ≈ sample. 5-6 standards & ASW blanks are digested.	KH_2PO_4 in DI water. Fresh standards & blanks are digested. Glycerophosphate check standard.	KH_2PO_4 in DI H_2O 5 standards - Are DI blanks and stds. digested?
Calibration Ranges	0.0186 - 0.092 & 0.1488 - 0.372 mg/L	0.005 - 0.15 mg/L	0.020 - 0.200 mg/L	0.010 - 0.500 mg/L
Calculated MDL	0.001 mg/L	0.001 - 0.004 mg/L	0.01 mg/L (1994) 0.001 mg/L (95-98)	0.01 mg/L
Lowest Standard	0.0186 mg/L	0.005 mg/L	0.020	0.010 mg/L
Number of splits with > 25% CV among replicates.	0/20	1/19	4/18	8/18
Std Ref Material % recovery range	SPEX 93-109	SPEX 90-104	APG 91-111	Not analyzed
CSSP spike% rec	**1994-1998** Range - 93-103 Mean – 97.9 Median – 97 **1997.5-1998** Range – 93 - 103 Mean – 98.3 Median –98.5	**1994-1998** Range - 90-105 Mean – 98.5 Median – 99 **1997.5-1998** Range – 93 - 105 Mean – 97.5 Median – 96.5	**1994-1998** Range - 78-104 Mean – 93.9 Median – 93 **1997.5-1998** Range – 93 - 99 Mean – 95.25 Median – 94.5	**1994-1998** Range - 81-105 Mean – 98.9 Median – 99.5 **1997.5-1998** Range – 94 – 101 Mean – 98.2 Median – 98

Hold. Time/Temp	≤ 28 days at -20°C	≤ 28 days at -20°C	≤ 28 days at -20°C	4°C for 48 hrs., or, ≤ 28 days w/ H_2SO_4

Split Results:

1994-1998

ANOVA results

Effect	*P Value*
Rep	0.86
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0001

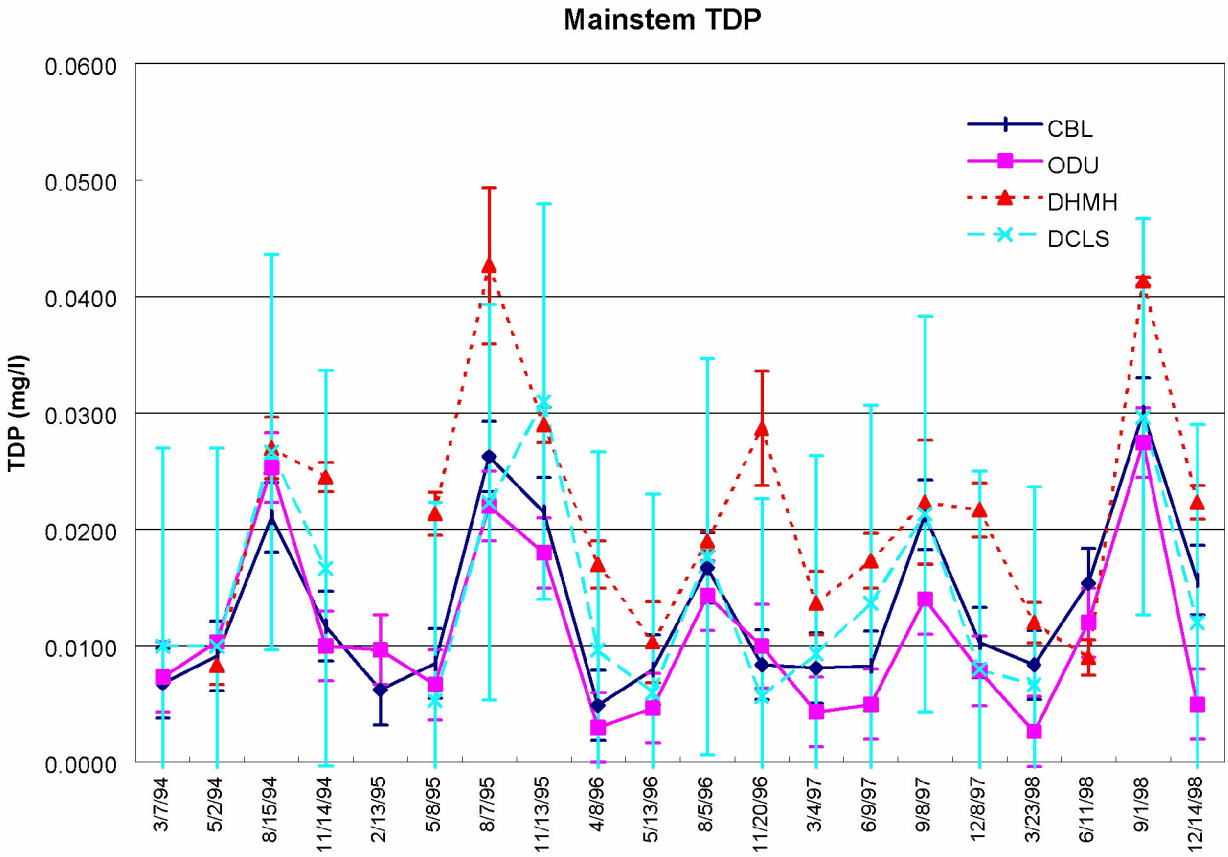
LS Means Results

Of Means	Of Residuals
DHMH DCLS CBL ODU	**CBL ODU DCLS DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. The remainder of the ANOVA results indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that ODU's TDP results were consistently different than the other three labs through time as was the case with DHMH. DCLS and CBL were not consistently different from one another (as indicated by the underlining below the two), but were different from ODU and DHMH. The LS Means of the residuals indicate that, in terms of variability around the mean, CBL and DHMH are different from one another but not from ODU and DCLS.

Graphical Results



Of the seventeen dates where all four labs had data, graphical results show that DHMH was significantly different than CBL and ODU twelve times. CBL, ODU and DCLS were not significantly different from one another and DCLS was not significantly different from DHMH.

Discussion of TDP Results

The results of the LS means analysis indicate that ODU is biased low and DHMH is biased high. This pattern can be seen in the graph of the data where ODU frequently has the lowest value on each date and DHMH almost always has the highest value. CBL and DCLS are always in the middle and do not appear to be consistently higher or lower than each other. No bias is indicated by the spike recoveries of ODU and DHMH; ODU's SRM recoveries are good. In June of 1997, ODU switched from a manual method using standard additions to an automated method but the methods were demonstrated to be equivalent. As of this date, ODU has not found the source of this apparent bias.

The LSM of the residuals indicate that CBL and DHMHs variability (precision) are significantly different. This is also evident upon examination of the CV data for both labs. Out of twenty observations, CBL had no CVs greater than 25% while DHMH had 8

of 18 greater than 25%. DHMH differences in variability may be due to using a block digestion procedure instead of the alkaline persulfate digestion.

The graphical analysis supports the differences detected between DHMH and CBL and DHMH and ODU by the LSM. It does not support the other differences detected by the LSM.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.2448
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0013

LS Means Results

Of Means

DHMH CBL DCLS ODU

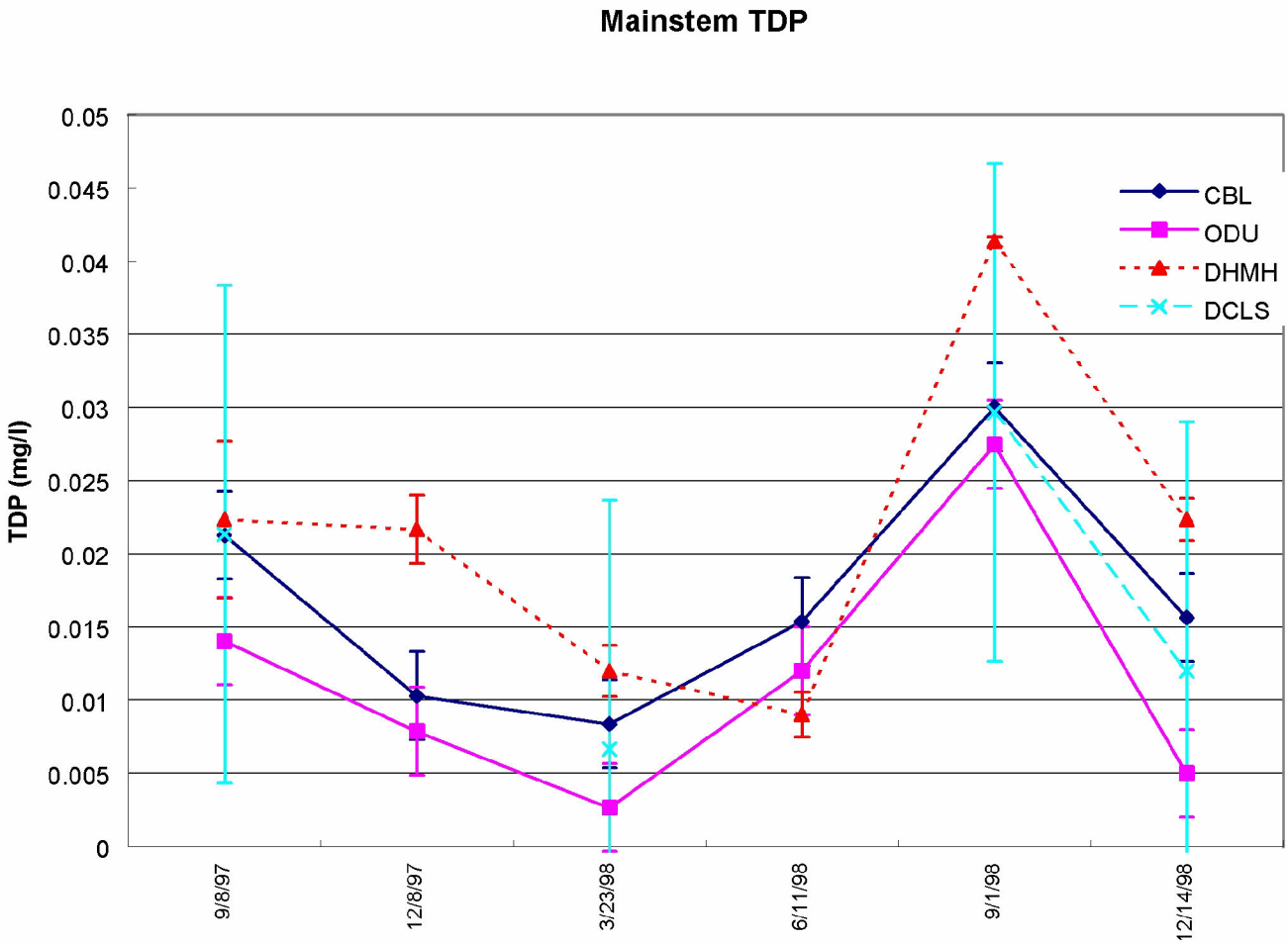
Of Residuals

CBL ODU DCLS DHMH

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. The remainder of the ANOVA results indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that ODU's TDP results were consistently different than the other three labs through time. DHMH was consistently different from DCLS and ODU but not from CBL. DCLS and CBL were not consistently different from one another but were from ODU. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences in variability among labs.

Graphical Results



On the four dates for which data were available for all labs, ODU was significantly different from DHMH on three out four dates. None of the other pairwise comparisons yielded significantly different results.

Discussion:

The negative bias detected in ODUs 1994-1998 data was also detected in the more recent 1997.5 – 1998 data. Also, examination of the graph of the 1997.5-1998 data indicates that DHMH still has a positive bias. The LSM of the residuals indicates that DHMHs precision improved in the 1997.5-1998 data set. The graphical analysis supports the difference between ODU and DHMH detected by the LSM but none of the other differences detected.

Parameter: Particulate Phosphorus

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL and ODU directly, DCLS indirectly until 2/95 and DHMH indirectly

Particulate Phosphorus Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS (after 2/95)	DHMH
Sample Filtration & Preparation	Particulates filtered in duplicate on 47 mm GF/F filters are dried at 104 °C, weighed for TSS and stored at room temp until combusted at 550°C for 1.5 hrs.	Particulates filtered on 47 mm GF/F, frozen at -20°C. Filters dried at 104°C, weighed for TSS, and combusted at 550 °C ≥ 1.5 hrs.	Particulates filtered on 47 mm GF/F, frozen until ready for analysis. Dried at 105°C overnight, muffled for 2 hours at 550°C. Cooled in desiccator.	Calculated PP = TP - TDP **TP** method is same as TDP (EPA 365.4, block digestion), using an un-filtered sample.
Method	Filters extracted in 1N HCl for ≤ 24 hrs before analysis. Combustion at 550°C converts all P cmpds. to PO_4, which is extracted w/ HCl and measured by EPA 365.1 (automated ascorbic acid method).	Cooled filters are extracted in 1N HCl for 24 hrs. Combustion at 550°C converts all P cmpds. to PO_4, which is extracted w/ HCl and measured by EPA 365.1 (automated ascorbic acid method).	*1/94 - 2/95*: Calculated 2/95 - present: Extracted overnight with 1N HCl, combust at 550°C to convert all P cmpds. to PO_4, which is extracted w/ HCl and measured by EPA 365.1	
Instrumentation	Technicon AAII 880 nm 50mm flow cell	1/94-12/95 SIC continuous flow analyzer. 1/96 on: SKALAR SAN^{plus} 880nm, w/ 1010nm background correction. 75mm flow cell, 40°C heat bath	SKALAR SAN^{plus} 880nm, w/ 1010nm background correction. 50mm flow cell	
Inst. Maintenance	DI rinse for 15 min.	Rinsed w/ RGW for 30 min. after analysis. Weekly: Cartridge cleaned w 0.5 N NaOH for hr. and RGW for hour. Align flowcell.	Rinsed w/ DI water daily. Rinsed w/ 0.5 N NaOH for hr. weekly	

Reagents	Two reagents, DI, SDS	1/94-12/95: Two reagents. 1/96 on: Combined reagent, RGW, SD-difenyl oxide disulfonates	Two reagents, FFD-6 wetting agent	
Standards & blanks	KH_2PO_4 in 1 N HCl	KH_2PO_4 in 1 N HCl	KH_2PO_4 in 1 N HCl Made fresh daily	
Calibration Ranges	0.185 - 1.48 mg/L	0.10 - 3.0 mg/L	0.010 - 0.500 mg/L	
Calculated MDL	0.0012 mg/L	0.0015 - 0.0034 mg/L	0.001 mg/L	0.02 mg/L (.01+ .01)
Lowest Standard	0.185 mg/L	0.10 mg/L	0.010 mg/L	Not Applicable
Number of splits with > 25% CV among replicates.	0/20 (all < 8% CV)	0/19 (all < 12% CV)	2/19	13/19 (7/19 > 50% CV)
Std Ref Material % rec. range	None	Spex aqueous 93-104	None	Not Applicable
CSSP spike %rec.	**1994-1998** Range – 96 - 103 Mean – 99.9 Median – 100 **1997.5-1998** Range – 100 - 103 Mean – 101.2 Median – 101	**1994-1998** Range – 92 - 110 Mean – 100.5 Median – 100.9 **1997.5-1998** Range – 97.8 – 106.5 Mean – 102.4 Median – 102.5	**1994-1998** Range – 96 - 113 Mean – 102.3 Median – 99 **1997.5-1998** Range – 96 - 110 Mean – 103.8 Median – 104.5	Not Applicable
Holding Time & Temperature	≤ 28 days at -20°C	≤ 28 days at -20°C	≤ 28 days at -20°C	Not Applicable

Split Analysis Results:

1994-1998

ANOVA results

Effect	*P Value*
Rep	0.18
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0064

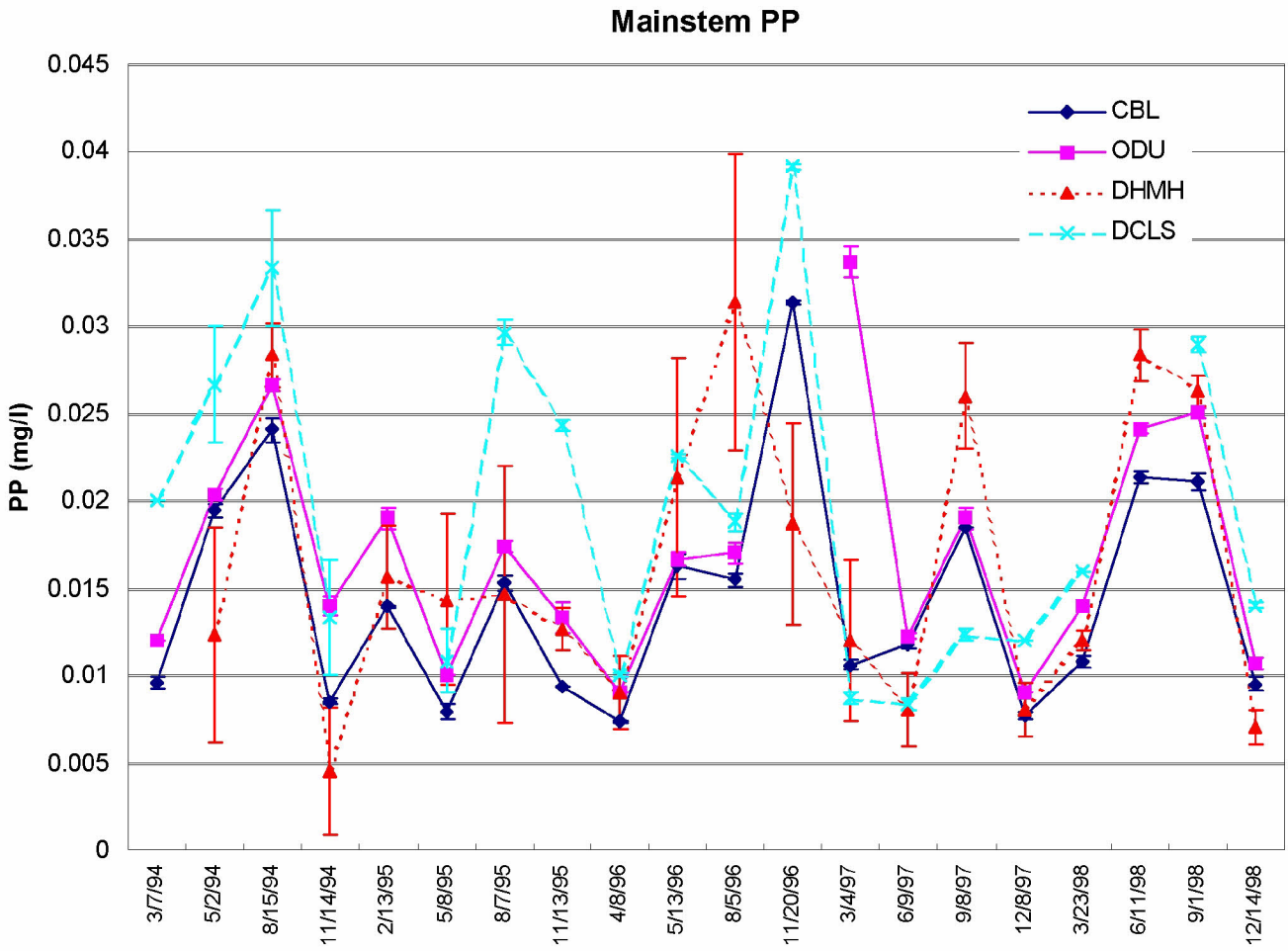
LS Means Results

Of Means	Of Residuals
DCLS ODU CBL DHMH	**ODU CBL DCLS DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. The remainder of the ANOVA results indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that there is good agreement among DCLS, ODU and CBL. DHMH's PP results were consistently different from DCLS and ODU but not from CBL. The LSM of the residuals indicate that, in terms of variability around the mean, DHMH was significantly different from the other three labs.

Graphical Results



Graphical results show that of the fourteen dates when data were available for all four labs, all labs were different from each other on more than 50% of those fourteen dates.

Discussion of Particulate Phosphorus

The difference detected by the LS means analysis between DCLS and DHMH and between ODU and DHMH may be due to the fact that DHMH calculates PP. This may also explain DHMHs high variability as detected by the LSM of the residuals and the number of CVs greater than 25%. No further causes were investigated.

While the LS means indicates good agreement among CBL, ODU and DCLS, the graphical analysis suggests that all of the labs are significantly different from one another. With the exception of DHMH, this may be due to the labs high precision with this parameter (as evidenced by their CVs and the results of the LSM of the residuals) which causes smaller error bars and reduces the likelihood of overlap.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.7829
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.4746

LS Means Results

Of Means

DCLS ODU DHMH CBL

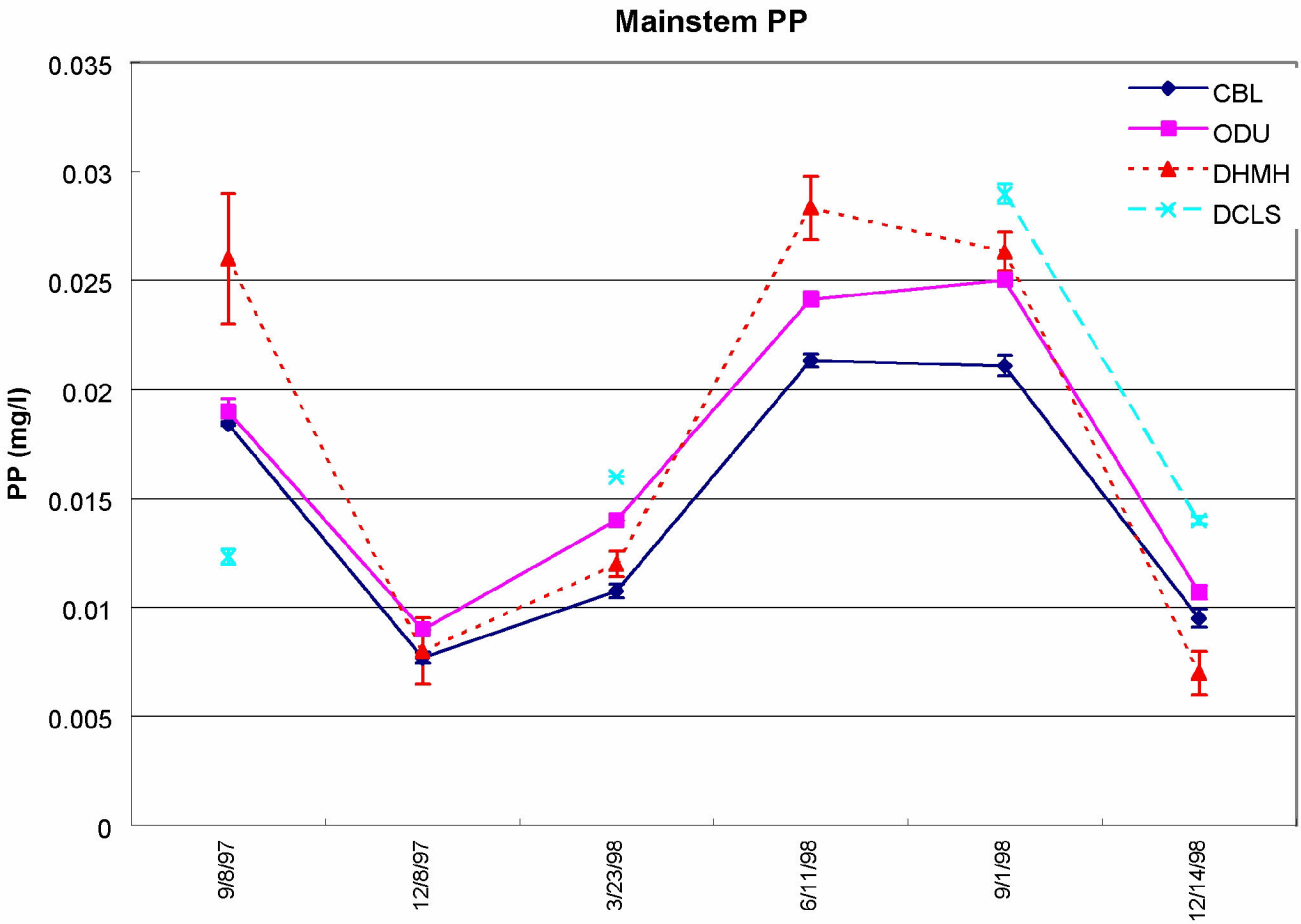
Of Residuals

DCLS ODU CBL DHMH

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. These results also indicate that there was a difference among labs, that this difference varied through time, but, that this difference was less than the within run variability associated with each lab.

The LS means results indicate that there were no consistent differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, DHMH was significantly different from the other three labs.

Graphical Results



Of the four dates when data were available for all labs, all labs were different from each other more than 50% of the time.

Discussion

The results indicate that from September 1997 through December 1998, there were differences among labs but that these differences do not appear to be consistent over time. This suggests and improvement for DHMH in the more recent data, however, the LSM of the residuals indicates that there is still a problem with precision. This may be due to the fact that DHMH calculates PP.

While the LS means results indicate that there were no consistent differences among labs, the graphical analysis suggests that all of the labs are significantly different from one another. With the exception of DHMH, this may be due to the labs high precision with this parameter (as evidenced by their CVs and the results of the LSM of the residuals) which causes smaller error bars and reduces the likelihood of overlap.

Parameter: Ortho-Phosphate

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Phosphate Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F in field, triplicate polystyrene AA cups.	Vacuum, 0.7μm GF/F in field HDPE,	Vacuum 0.7μm GF//F in field, HDPE.	Vacuum, 0.7μm GF/F in field, HDPE
Glassware	Cleaned w/ 10% HCl, DI rinsed	Class A volumetric. *1/94-5/97*: Dichromic acid soak w/ RGW rinse. *6/97 on*: Liquinox , w/ tap water rinse, rinsed twice w/ 4N HCl then 9 X w/ RGW	Dedicated glassware washed in 1:1 HCl, DI rinsed.	Dedicated glassware, washed in 1:1 HCL, DI rinsed.
Method	EPA 365.1/EPA 365.5 automated ascorbic acid method. Refractive Index Salinity Correction	*1/94-5/97*: EPA 365.3 Manual ascorbic acid by std. addition. *6/97 on*: EPA 365.1/ 365.5: auto. ascorbic acid method.	EPA 365.1: automated ascorbic acid method.	EPA 365.1: automated ascorbic acid method. Refractive Index Salinity Correction
Instrumentation	Technicon AAII; 880 nm 50 mm flow cell	*1/94-5/97*: Perkin Elmer λ-1 single beam spec. *6/97 on*: Skalar SAN^{plus}, 880nm. Auto background/ matrix correct (1010nm) 75 mm flow cell, 40°C heat bath	Skalar SAN^{plus}, 880nm. Auto background/ matrix correction w/ 1010nm filter. 50 mm flow cell	Alpkem model 3570 with SoftPac software, 660 nm, 5mm flow cell 37°C (or 50°C?) heat bath.
Inst. Maintenance	Rinsed w 0.1 N HCl for 5 min. after analysis, DI for 15 min.	Rinsed w/ RGW for 30 min. after analysis. Weekly: Cartridge cleaned w 0.5 N NaOH for hr. and RGW for hour. Align flowcell. 0	Rinsed w/ DI water daily. Rinsed w/ 0.5 N NaOH for hr. weekly	Rinse w/DI for 15 min, 15 min w/10% HCL, 20 min with DI, 30 min with 1N NaOH, 30 min w/DI water.

Reagents	Two reagents, DI, SDS	Combined reagent, DI, SD-difenyl oxide disulfonates	Two reagents, FFD-6 wetting agent	Two reagents, DI?or Dowfax 2A!?
Standards & blanks	KH_2PO_4 in DI H_2O	*1/94-5/97*: KH_2PO_4 in com-posite of filter. sample water. *6/97 on*: ASW salinity ≈ sample. 5-6 standards & ASW blanks for std. curve.	KH_2PO_4 in DI H_2O Made fresh daily	KH_2PO_4 in DI H_2O Working stds in dem. Water.
Calibration Ranges	0.00372 - 0.372	0.002 - 0.08 mg/L	0.010 - 0.100 mg/L	0.004 - 0.3 mg/L
Calculated MDL	0.0006 mg/L	0.0003 - 0.003 mg/L	0.002 mg/L	0.0012 - 0.0017 mg/L
Lowest Standard	0.00372 mg/L	0.002 mg/L	0.010	0.004 mg/L
Number of splits with > 25% CV among replicates.	9/20 (4/20 > 50% CV)	2/14	1/17	3/18
Std Ref Material % recovery range	SPEX 93-109	SPEX 75-110 *(1/94 - 5/97)* 97-102 *(6/97 on)*	APG 77-107	88-109
CSSP spike % recovery range	**1994-1998** Range – 92 - 104 Mean – 98.4 Median – 97.5 **1997.5-1998** Range – 92 - 103 Mean – 97.3 Median – 96.5	**1994-1998** Range – 86 - 103 Mean – 95.3 Median –95.5 **1997.5-1998** Range – 90 - 98 Mean – 97.5 Median – 96.5	**1994-1998** Range – 85 - 102 Mean – 93.9 Median – 94 **1997.5-1998** Range – 91 – 95 Mean – 92 Median – 91	**1994-1998** Range – 78 – 102 Mean – 94.9 Median – 98 **1997.5-1998** Range – 92 – 100 Mean – 98.3 Median – 100

Holding Time & Temperature	≤ 28 days at -20°C	4°C ~ 4 hrs., frozen -20°C ≤ 28 days	4°C ~ 24 hrs, frozen at -20°C ≤ 28 days	4°C ≤ 48 hrs.

Split Results:

1994-1998

ANOVA results

Effect	*P Value*
Rep	0.8741
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0066

LS Means Results

Of Means

DHMH DCLS CBL ODU

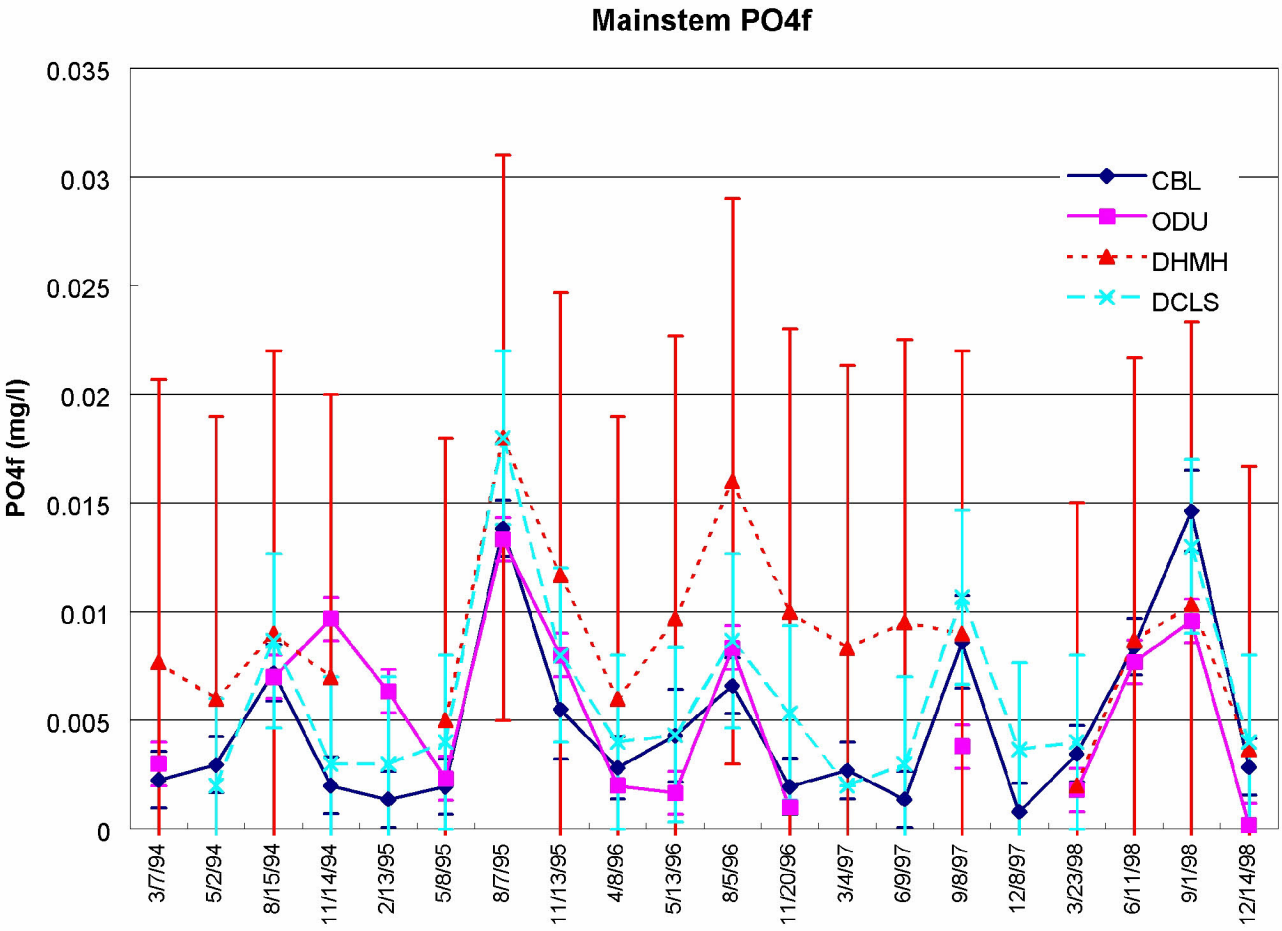
Of Residuals

DCLS ODU DHMH CBL

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DHMH and ODU were consistently different from each other. The LS Means of the residuals indicate that, in terms of variability around the mean, CBL was significantly different from the other three labs.

Graphical Results



The graphical analysis did not reveal any pairwise differences among labs occurring on more than 50% of the dates where there were data available for all labs. Visual inspection shows that DHMH frequently has a high bias relative to the other labs with very large error bars.

Discussion of Orthophosphate

The LS means analysis indicates that there is a significant bias between ODU and DHMH. (This was also the case for TDP.) The bias can be seen in the graph above where DHMH generally has higher values for PO4f and ODU generally has lower values. These graphical differences, however, are not statistically significant. These biases are not apparent in the percent recovery data.

Differences in DHMH results prompted an investigation that revealed they had not corrected for salinity (refractive index correction). Corrections were calculated and applied to the database in 1998.

ODU investigated their method but did not find any reason for their differences.

The LSM analysis of the residuals indicate that CBL has significant variability around the mean. This is supported by the CV where nine out of CBL's twenty observations were greater than 25%.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.0628
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0582

LS Means Results

Of Means

DCLS CBL DHMH ODU

Of Residuals

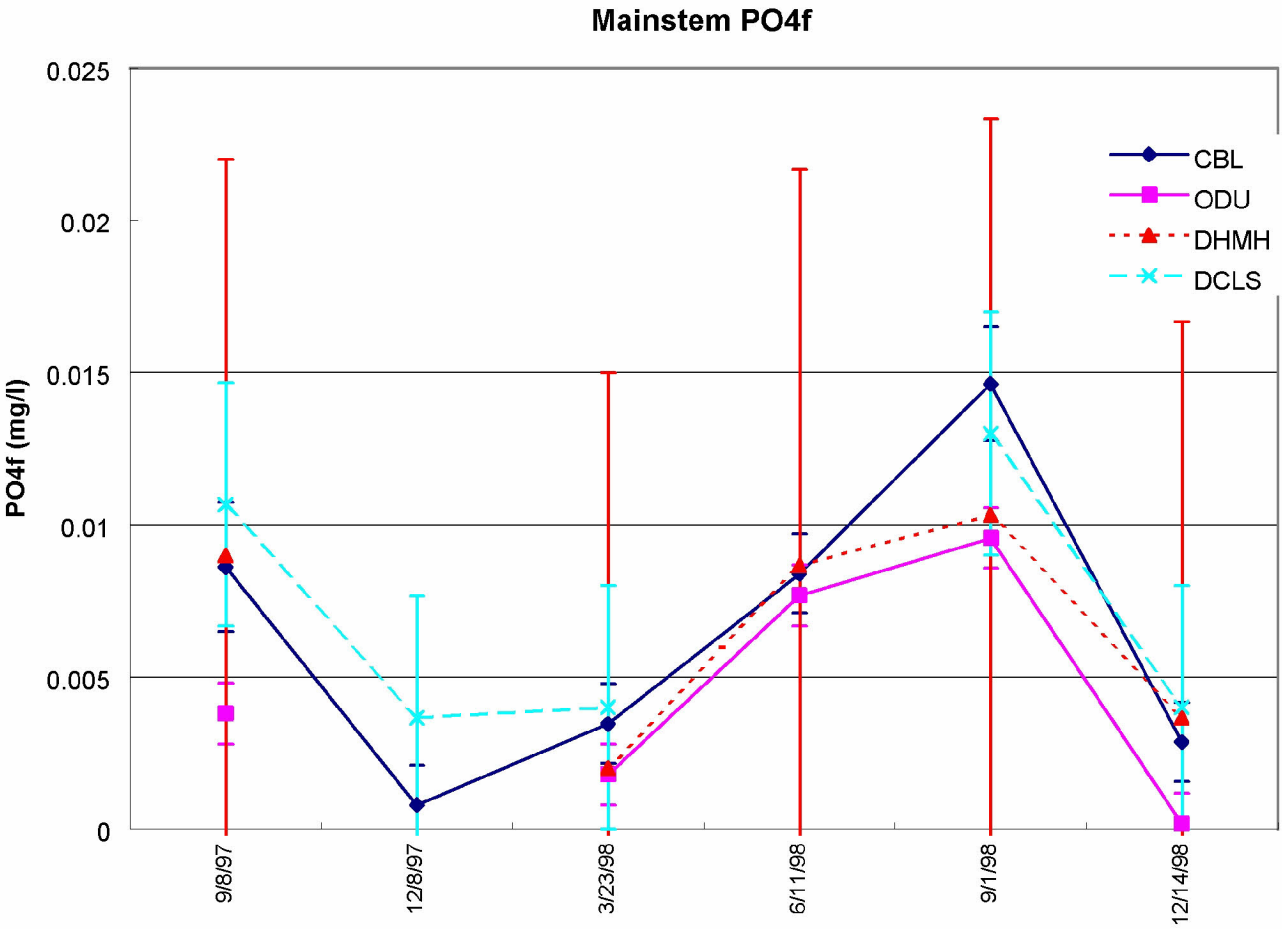
DCLS DHMH ODU CBL

The ANOVA results indicate that there is no replicate affect on variability within the data meaning the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there are no consistent differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, CBL was significantly different from the other three labs.

The graphical analysis found no differences among labs.

Graphical Results



Results of the graphical analysis indicate that CBL is different from ODU on three out of the four dates where data were available for all four labs.

Discussion

The LSM analysis found no significant differences among labs in the 1997.5-1998 data. The graphical analysis did find a significant difference between CBL and ODU. This is due to both labs relatively small error bars.

The LSM of the residuals indicates that CBL still exhibits significant variability about the mean in the more recent data set.

Parameter: Total Phosphorus

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL and ODU measure indirectly (TDP + PP). See these parameters for method descriptions. DHMH and DCLS measure total phosphorus directly. (Note: TDP and PP are reported to the Chesapeake Information Management System.) DCLS's results from the direct measurement are compared below.

DHMH analyzes total phosphorus using EPA Method 365.4. The automated, colorimetric method is the same as that used for Total Dissolved Phosphorus, only an unfiltered sample is analyzed. (See TDP section for details.) Samples are digested at 360 C using sulfuric acid, K_2SO_4 and $HgSO_4$ for several hours in a block digestor. The residue is cooled, diluted and placed on an AutoAnalyzer and analyzed by the ascorbic acid method.

DCLS analyzes total phosphorus using EPA Method 365.1. In saline waters, the method is the same as that used for Total Dissolved Phosphorus, only an unfiltered sample is analyzed. (See TDP section for details.) Samples are digested using a manual acid persulfate digestion because high percent recoveries occur in saline samples with the block digestor. Digested samples are analyzed on a Skalar autoanalyzer.

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.9468
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0002

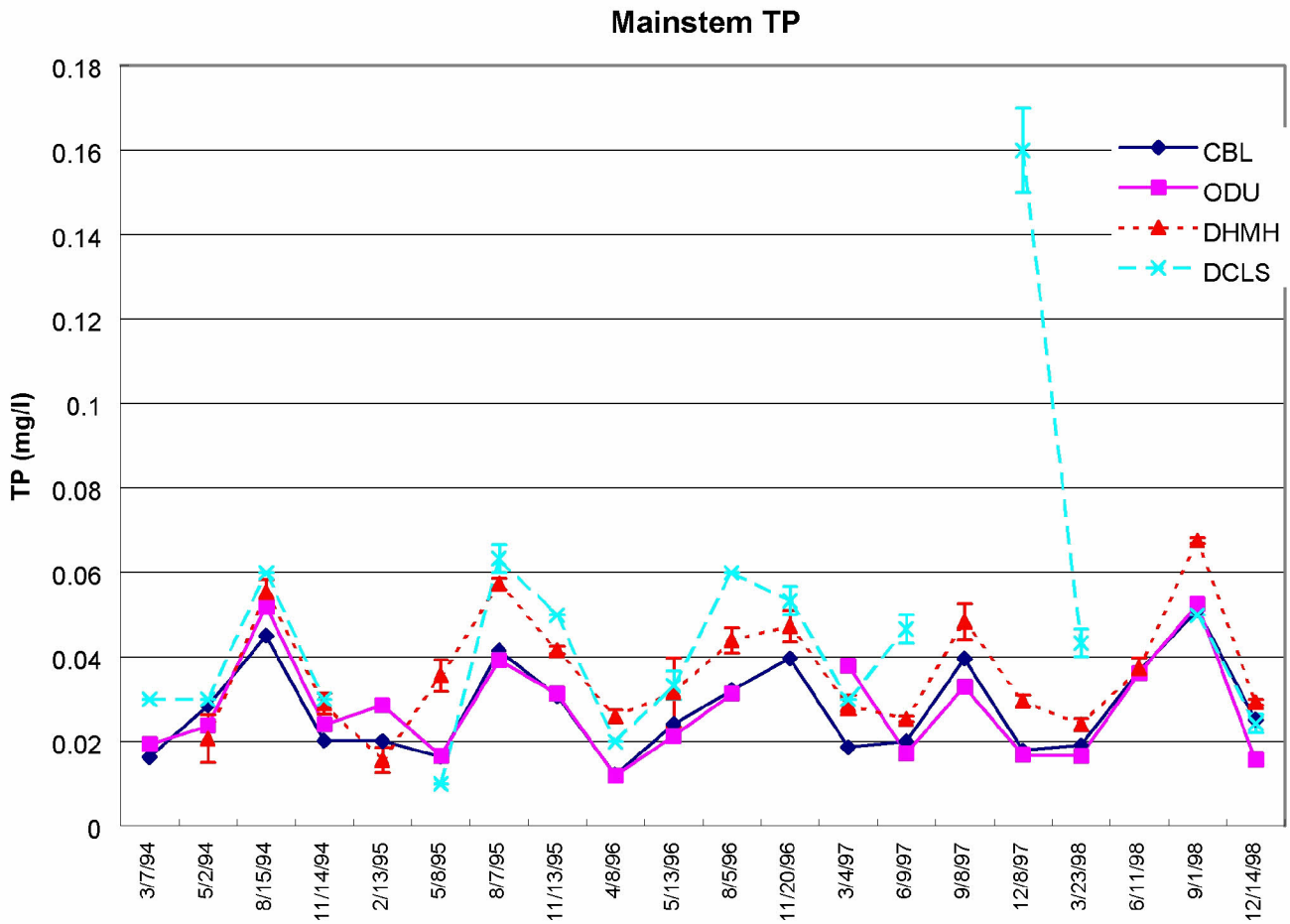
LS Means Results

Of Means	Of Residuals
DHMH DCLS CBL ODU	**CBL DCLS ODU DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data, which means that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DHMH was consistently different from CBL and ODU and ODU was consistently different from DCLS and DHMH. The LS Means of the residuals indicate that, in terms of variability around the mean, DHMH was significantly different from CBL and DCLS.

Graphical Results



Graphical analysis shows that of the fifteen dates where data are available for all labs, only CBL and ODU were not different than each other on more than 50% of the dates.

Discussion of TP results

The differences between the labs detected by the LS means may be due to the fact that CBL and ODU calculate TP and DCLS and DHMH measure it directly.

The result from the graphical analysis that CBL and ODU are not significantly different from one another is supported by the same result from the LS means.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.5107
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.1299

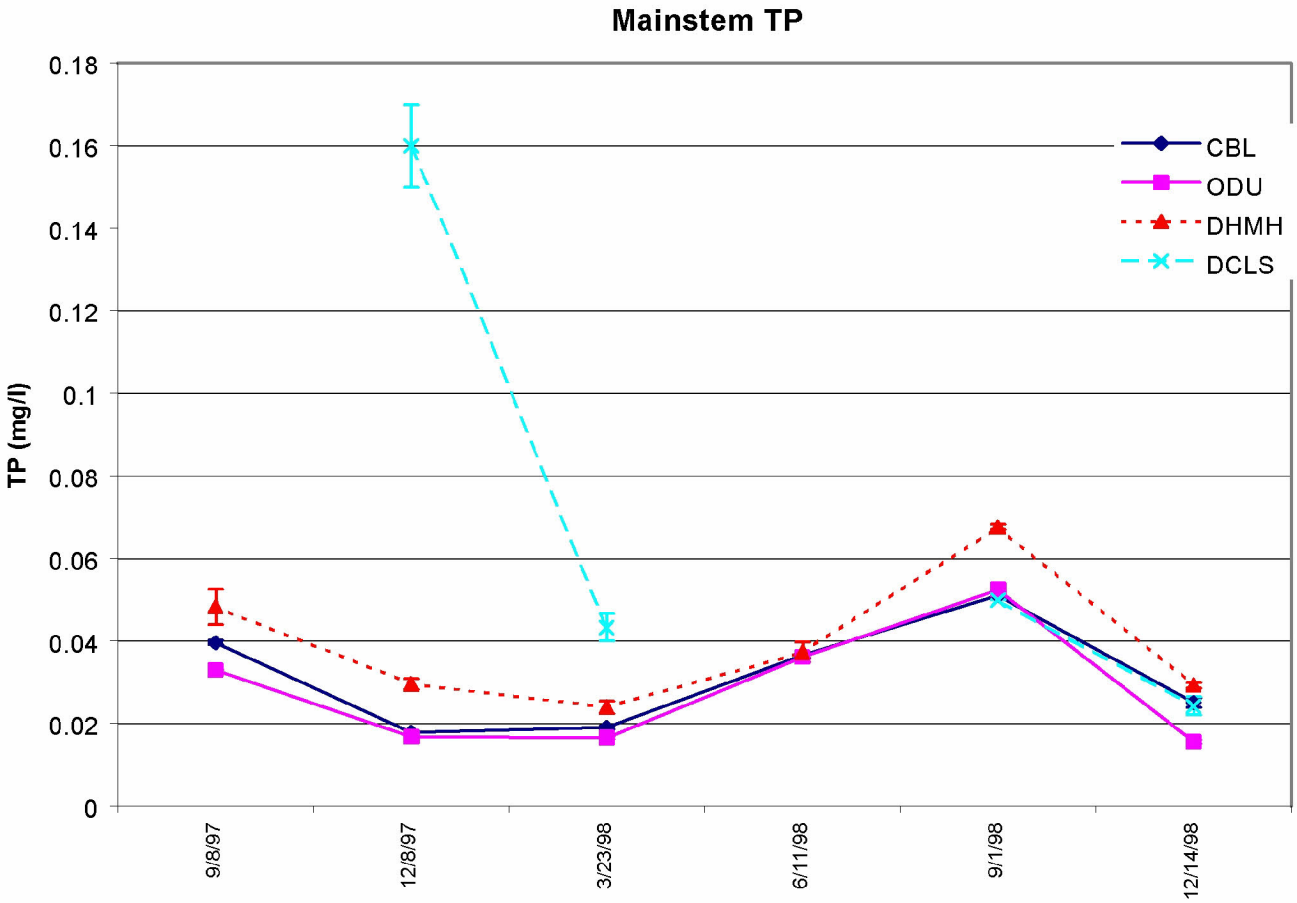
LS Means Results

Of Means	Of Residuals
DCLS DHMH CBL ODU	**ODU CBL DHMH DCLS**

The ANOVA results indicate that there is no replicate affect on variability within the data, which indicates that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no consistent differences among labs. The LSM of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the four dates where data were available for all labs, all labs were different from one another on more than 50% of the dates.

Discussion

Although no biases were detected by the LS means test, viewing the data graphically indicates two potential problem areas. First, DCLS recorded drastically higher values for the December 1997 and March 1998 cruises. Second, DHMH's results appear to be consistently higher relative to the other labs.

The results of the graphical analysis are not supported by the results of the LS means.

Parameter: Total Dissolved Nitrogen

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL, ODU and DCLS measure directly, DHMH measures indirectly (TKNf + NO23)

Total Dissolved Nitrogen Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F 30 ml glass test tube	Vacuum, 0.7μm GF/F HDPE, 250 ml	Vacuum, 0.7μmGF/F HDPE	Vacuum,0.7μmGF/F HDPE
Glassware	Graduated cylinders. Glass tubes cleaned w/ 10% HCl, DI rinsed. autoclaved with potassium persulfate before use.	Class A volumetric. Dedicated glass tubes. Liquinox , w/tap water rinse, rinsed twice w/ 4N HCl then 9 times w/ RGW.	Rainin auto pipet. Digestion tubes autoclaved with persulfate before use. Dedicated glassware washed in 1:1 HCl, DI rinsed.	
Method	Alkaline persulfate digestion (60 @ 4psi) + EPA 353.2- automated cadmium reduction method. (Valderrama, 1981&D Elia et.al, 1977)	Alkaline persulfate digestion (autoclave 30min @ 105 EC) + EPA 353.2 - automated cadmium reduction method.	Alkaline persulfate digestion + EPA 353.2 automated cadmium reduction.	Calculated: TKN + (NO_2 + NO_3).
Instrumentation	Technicon AAII; 550 nm filter photometer. 50 mm flow cell	1/94-12/95: SIC continuous flow analyzer. 1/96 on: Skalar SAN^{plus}, 540 nm filter photometer with 620 nm background correction. 75 mm flow cell	Skalar SAN^{plus}, 540nm filter photometer with 620 nm background correction. 50 mm flow cell	Not applicable
Inst. Maintenance	Rinsed w 1N HCl for 15 min. after analysis, DI for 15 min.	Rinsed w/ RGW for 30 min. after analysis. Weekly: Cartridge cleaned w 1% hypochlorite sol n for hr. and RGW for hour. Align flowcell.	Rinsed w/ DI water daily. Rinsed w/ 1N HCl weekly, 1% hypo-chlorite weekly	Not applicable

Reagents	Potassium persulfate, boric acid buffer digest.	Potassium persulfate ($K_2S_2O_8$) boric acid buffer digestion	Potassium persulfate, boric acid buffer digest	Not applicable
Standards	1) KNO_3, dried at 45 °C (also used to check cadmium column) 2) Glutamic acid internal standard All diluted with DI water and digested.	1) KNO_3, dried at 103°C & standardized 2) $NaNO_2$, dried (to check cadmium column) 3) Glutamic acid internal std. All diluted with ASW water and digested.	1) KNO_3, dried at 105°C 2) Urea check standard Prepared fresh daily in DI water. Standards & blanks are digested.	Not applicable
Calibration Ranges	0.35 - 1.05 mg/L 2.1 - 5.6 mg/L	0.025 - 1.0 mg/L	0.100 - 1.000 mg/L	Not applicable
Calculated MDL	0.02 mg/L	0.0096 - 0.025 mg/L	0.004 mg/L	0.1(TKN + NO_2 +NO_3)
Lowest Standard	0.35 mg/L	0.025 mg/L	0.100 mg/L	Not applicable
Number of splits with > 25% CV among replicates.	0/20	0/20	0/14	0/16
Std Ref Material % recovery range	100-112	94-104	95-104	TKN: 86-103 NO_2 +NO_3: 96-108
CSSP spike% rec	**1994-1998** Range – 95 – 108 Mean – 99.7 Median – 99 **1997.5-1998** Range – 95 – 108 Mean – 101.2 Median – 100.5	**1994-1998** Range – 89 - 118 Mean – 101 Median – 100 **1997.5-1998** Range – 98 – 101 Mean – 100 Median – 100	**1994-1998** Range – 62 – 103 Mean – 91 Median – 93 **1997.5-1998** Range – 89 – 103 Mean – 95.5 Median –95	**TKNw 1994-1998** Range – 90 – 116 Mean – 105.2 Median – 106.5 **TKNw 1997.5-1998** Range – 90 – 101 Mean – 95.8 Median – 97 (see NO2+3 values)

Holding Time	≤ 28 days at -20°C	≤ 28 days at -20°C	≤ 28 days at -20°C	Not applicable

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.5346
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0201

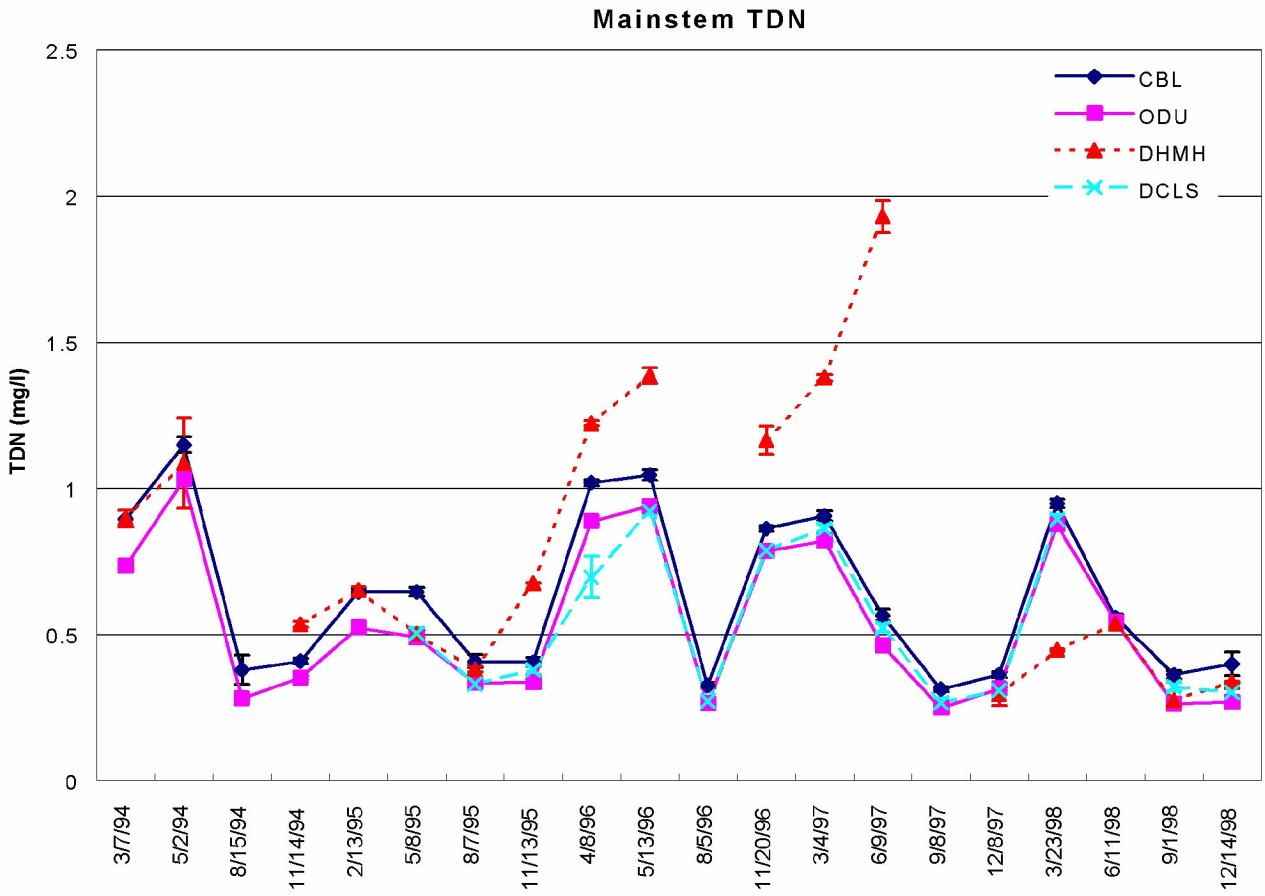
LS Means Results

Of Means	Of Residuals
DHMH CBL DCLS ODU	**ODU DCLS DHMH CBL**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DHMH was consistently different from ODU. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



On the 12 dates for which data were available, only ODU and DCLS were not different from each other on more than 50% of the dates.

Discussion of TDN

The LS means analysis indicates that there is a significant bias between ODU and DHMH. This difference may be due to the fact that DHMH calculates TDN and ODU measures it directly. Other causes of the differences were not investigated. The difference between ODU and DHMH is supported by the graphical results.

It would appear that, relative to each other, none of the labs have a problem with variability around the mean. This is supported by the CV data.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.2954
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.1202

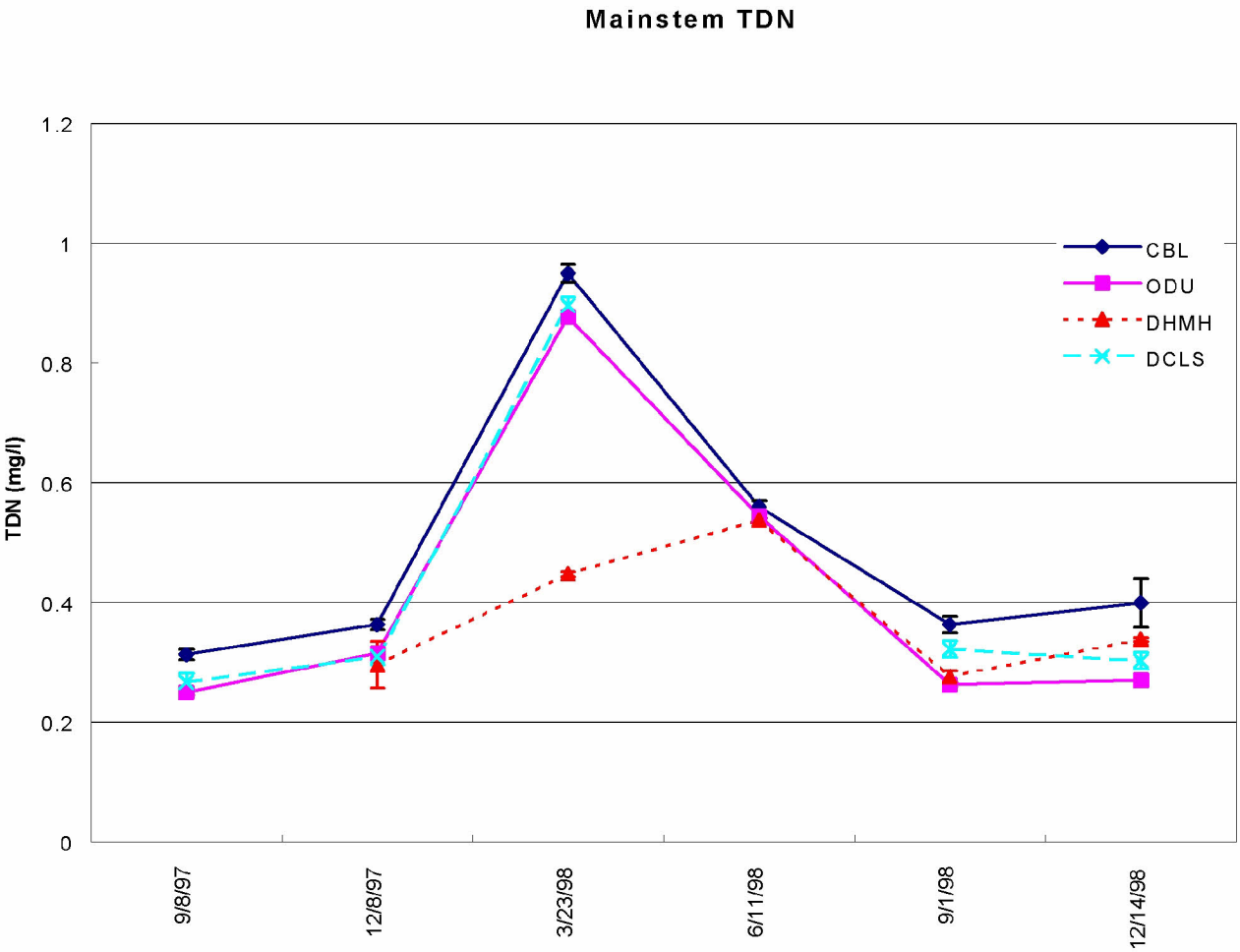
LS Means Results

Of Means	Of Residuals
CBL DCLS ODU DHMH	**ODU DCLS DHMH CBL**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there are no consistent differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Graphical results show that of the four dates where data were available for all labs, CBL was always different from the other labs and DLCS and DHMH were different on three of the four dates.

Discussion

Although it was undetected in the LSM analysis, after review of the graphical results it would appear that CBL has a slight positive bias. This positive bias is supported by the SRM percent recovery data in which all values were 100% or greater.

The differences detected in the graphical analysis are not supported by the LSM analysis.

Parameter: Particulate Nitrogen

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL, ODU and DCLS measure directly, DHMH does not measure.

Particulate Nitrogen Method Comparison- Mainstem Labs

Variable	CBL	ODU	DCLS (after 2/95)	DHMH
Sample Filtration & Preparation	1) 25 mm GF/F muffled at 550C for 90 min. 2) Particulates are field filtered in duplicate, placed in Al foil pouch. 3) Filters dried at 45 °C overnight	1) 13 mm GF/F & glass vials are muffled at 550C for 15 min & 4 hrs respectively. 2) Particulates are field filtered ≤ 50 mL sample on 13 mm GFF, placed in glass vials. 3)Filters dried at 50°C over-night, dessicated. After 6/97, no chloroform/methanol cleaning of tin sample cups.	1) 25mm Gelman glass fiber filters 2) 25ml-250ml sample (visible color on pad) 3) Filtlers dried over-night at 50°C Sample cup precombust at 875°C for 1 hr.	Calculated PN = TKNW - TKNF EPA Method 351.2, Semi-automated, block digestor, nitroprusside.
Method	Filters & Al capsule placed into nickel sleeves & combusted at 975°C. NO_X cmpds are reduced to N_2(g).	Filters placed into tin sample cups are flash combusted at 1040°C. A series of catalytic and Cu reducing reactors convert NO_X cmpds to N_2(g),	Combusted at 990°C	
Instrumentation	Exeter CE-440 Elemental Analyzer w Cu reduction column, He carrier gas & thermal conductivity detector.	Carlo Erba C/N gas chromat-ograph equipped with combustion & Cu reduction columns, He carrier gas & a thermal conductivity detector.	Exeter Model CE-440 Elemental Analyzer, Cu reduction column, He carrier gas & thermal conductivity detector.	
Inst. Maintenance	Columns renewed after 300-600 samples	Columns renewed after 300-600 samples		

Reagents	Helium carrier gas	Helium carrier gas		
Standards	1.5 mg acetanilide (10.36%N)	Chloramine-T dried for 30 min. at 50°C	Acetanilide	
Calibration Ranges	None: standards run as recovery check.	0.05 mg - 1.0 mg 5 pt. calibration curve	None: standards run as recovery check.	
Calculated MDL	0.0123 mg/L	0.007 - 0.0414 mg/L	0.01 mg/L	0.114 mg/L (0.057+ 0.057)
Lowest Standard	None	0.05 mg	None	Not applicable
Number of splits with > 25% CV among replicates.	0/20 (all < 4.5% CV)	2/18	0/10	Not applicable
Std Ref Material % rec. range	None	None	None	None
CSSP spike% rec	None	None	None	None
Holding Time & Temperature	≤ 28 days at -20°C	≤ 28 days at -20°C		4 °C ≤ 48 hours

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.5814
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0092

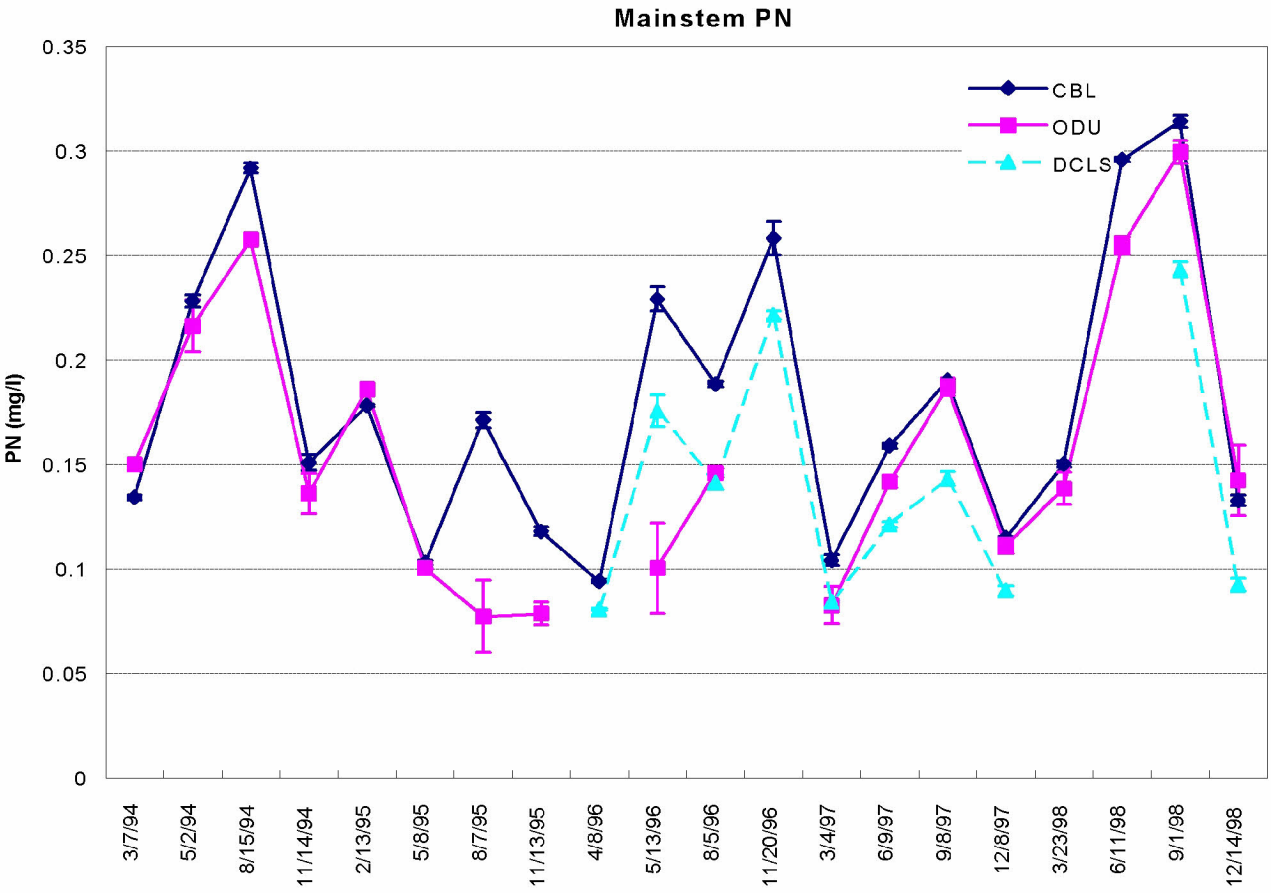
LS Means Results

Of Means	Of Residuals
CBL ODU DCLS	**CBL DCLS ODU**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that CBL and DCLS were consistently different. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Graphical results show that of the eight dates when were data available for all three labs, all labs failed the pairwise comparisons.

Discussion of Particulate Nitrogen

From June 1997 on, DCLS was consistently lower than CBL and ODU indicating the development of a negative bias. This cause of this needs to be investigated. The graphical analysis indicated that DCLS and CBL were significantly different from each other, which is supported by the LSM.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.4268
Lab	0.0001
Date*Lab	0.1961
Lab using Date*Lab error term	0.0003

LS Means Results

Of Means

CBL ODU DCLS

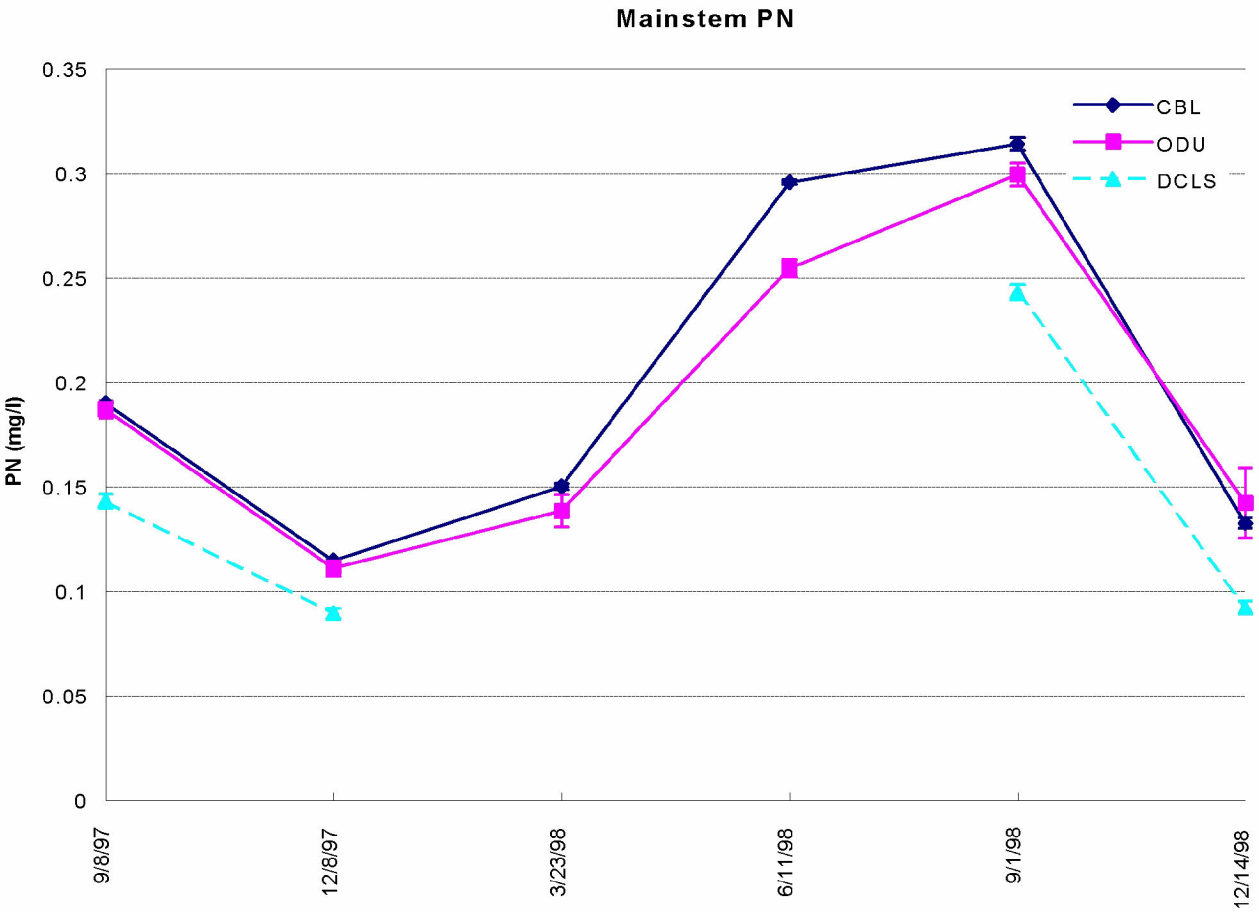
Of Residuals

CBL DCLS ODU

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference was not variable through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DCLS was consistently different from CBL and ODU. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the four dates when data were available for all labs, DCLS was different from CBL and ODU on all dates.

Discussion

It appears from both the LSM and the graphical analysis that DCLS has a negative bias. This supports the suggestion in the 1994-1998 analysis that DCLS was developing a negative bias.

Parameter: Ammonium

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Ammonium Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F in field, triplicate polystyrene AA cups	Vacuum, 0.7μm GF/F in field HDPE	Vacuum 0.7μm GF/F in field, HDPE.	Vacuum, 0.7μm GF/F in field, HDPE
Glassware	Cleaned w/ 10% HCl, DI rinsed	Liquinox , w/ tap water rinse, rinsed twice w/ 4N HCl then 9 times w/ RGW	Washed in 1:1 HCl, DI rinsed.	Washed in 1:1 HCL, DI rinsed.
Method	EPA 350.1, automated phenate method. (Berthelot Reaction)	EPA 350.1, automated phenate method. (Berthelot Reaction)	EPA 350.1, automated phenate method. (Berthelot Reaction)	EPA 350.1, automated phenate method. (Berthelot Reaction)
Instrumentation	Technicon TrAAcs-800 630 nm 37 °C heating bath 50 mm flow cell	*1/94-5/97*: SIC continuous flow analyzer. *6/97 on*: Skalar SAN^{plus}, 630 nm. Auto background/ matrix correct (1010 nm filter) 75 mm flow cell, 40°C heat bath	Skalar SAN^{plus}, 630nm. Auto background/ matrix correction w/ 1010nm filter. 50 mm flow cell	Alpkem model 3570 with SoftPac software, 660nm, 5 mm flow cell
Inst. Maintenance	Rinsed w 1N HCl for 15 min. after analysis, DI for 15 min.	Daily: Rinse w RGW for 30 min. Weekly: Clean cartridge w 10% hypochlorite (hr), RGW rinse (hr). Align flow cell.	Rinsed w/ DI daily, w/ 1 N HCl weekly	Daily rinse w/DI for 15 min, rinse with 10% HCL, rinse w/DI 30min.
Reagents	Tartrate/Citrate Complexing Reagent w/ Brij-35, alk. phenol, NaClO, Nitroprusside	Tartrate/Citrate Complexing Reagent w/ Brij-35, alkaline phenol, NaClO, Nitroprusside	Tartrate/Citrate Complexing Reagent w/ Brij-35, alk. phenol, NaClO, Nitroprusside	Tartrate/Citrate Complexing Reagent w/ Brij-35, alk. phenol, NaClO, Nitroprusside
Standards	$(NH_4)_2SO_4$ dried @ 45°C $CHCl_3$ preservative in stock sol n	$(NH_4)_2SO_4$ dried @ 103°C Working stds. diluted with artificial sea water.	$(NH_4)_2SO_4$ dried @ 105°C Prepared fresh daily in DI water	NH_4Cl dried @103°C, working stds diluted w/dim water.

Calibration Ranges	0.021 - 0.168 mg/L	0.005 - 0.15 mg/L	0.010 - 0.100 mg/L	0.008 - 0.6 mg/L
Calculated MDL	0.003 mg/L	0.0007 - 0.0025 mg/L	0.004 mg/L	0.0015-0.0017 mg/L
Lowest Standard	0.021 mg/L	0.005 mg/L	0.010 mg/L	0.008 mg/L
Number of splits with > 25% CV among replicates.	7/20 (6/20 > 50% CV)	4/19 (all > 50% CV)	2/18	3/19 (all > 50% CV)
Std Ref Material % recovery range	94-111	94-110	92-114	94-107
CSSP spike % recovery range	**1994-1998** Range – 88 – 106 Mean – 96.4 Median – 96.5 **1997.5-1998** Range – 93 – 99 Mean – 96.5 Median – 96.5	**1994-1998** Range – 91 – 109 Mean – 101.9 Median – 104 **1997.5-1998** Range – 99 – 109 Mean – 105.8 Median – 108	**1994-1998** Range – 85 – 153 Mean – 106.1 Median – 105 **1997.5-1998** Range – 90 – 110 Mean – 100 Median –100	**1994-1998** Range – 91 - 106 Mean – 98.4 Median – 98 **1997.5-1998** Range – 93 – 106 Mean – 100.3 Median – 101
Holding Time & Temperature	≤ 28 days at -20°C	4°C ~ 4 hrs., frozen at -20°C < 28 days	4°C ~ 24 hrs, frozen at -20°C ≤ 28 days	4°C for 48 hrs.

Split Results:

1994-1998

ANOVA results

Effect	*P Value*
Rep	0.0922
Lab	<0.0001
Date*Lab	<0.0001
Lab using Date*Lab error term	0.5056

LS Means Results

Of Means

CBL ODU DHMH DCLS

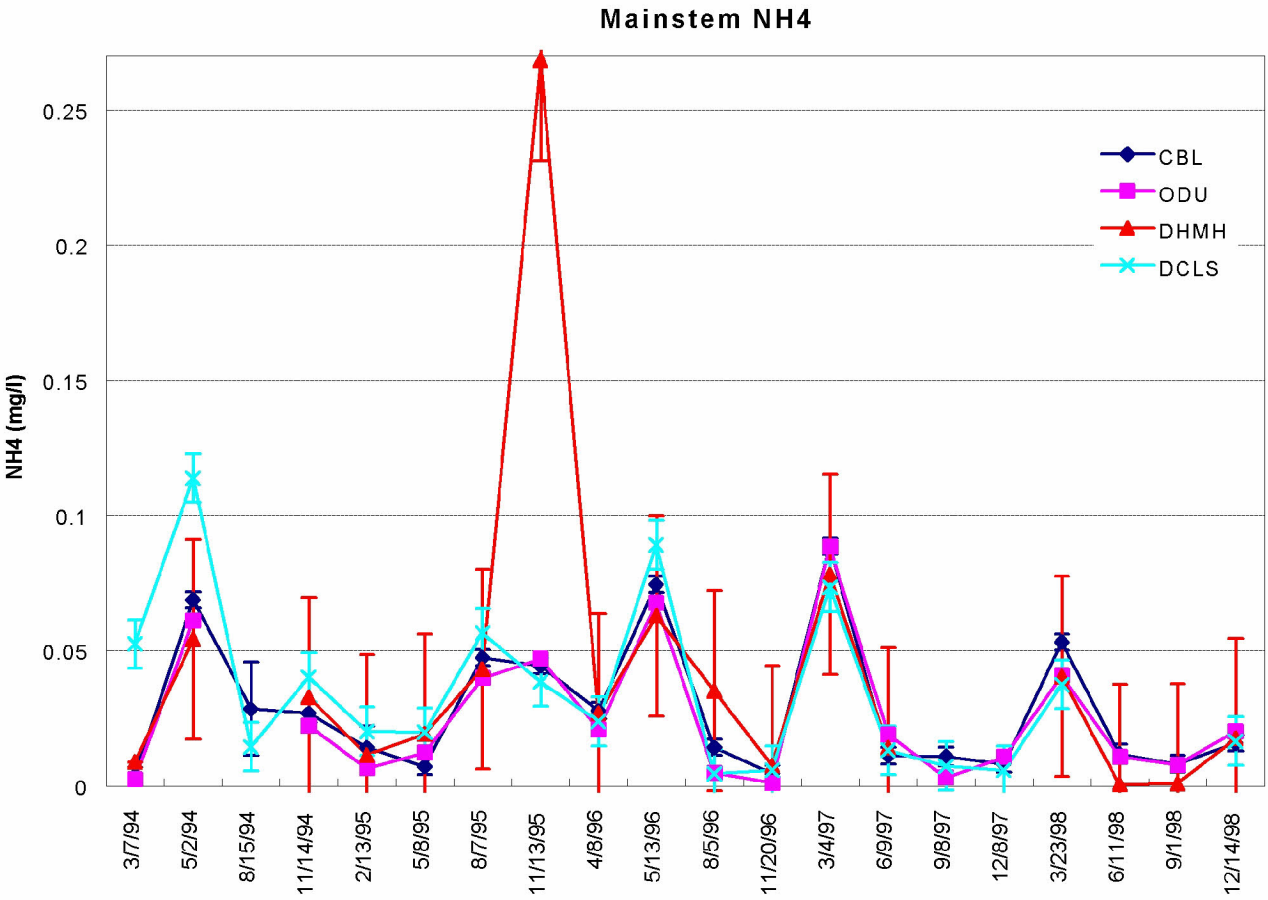
Of Residuals

CBL DHMH DCLS ODU

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the 15 dates for which data from all four labs were available, no pairwise comparisons resulted in labs being different from one another on more than 50% of the dates.

Discussion of Ammonium

Although no biases or differences were detected it should be noted that on three dates (11/95, 9/97 and 12/97) DHMH had results that were an order of magnitude higher than the other labs. The 9/97 and 12/97 results were removed from the analyses because all of DHMH ammonia data during that period was deleted from the data base.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.2386
Lab	0.0023
Date*Lab	<0.0001
Lab using Date*Lab error term	0.7359

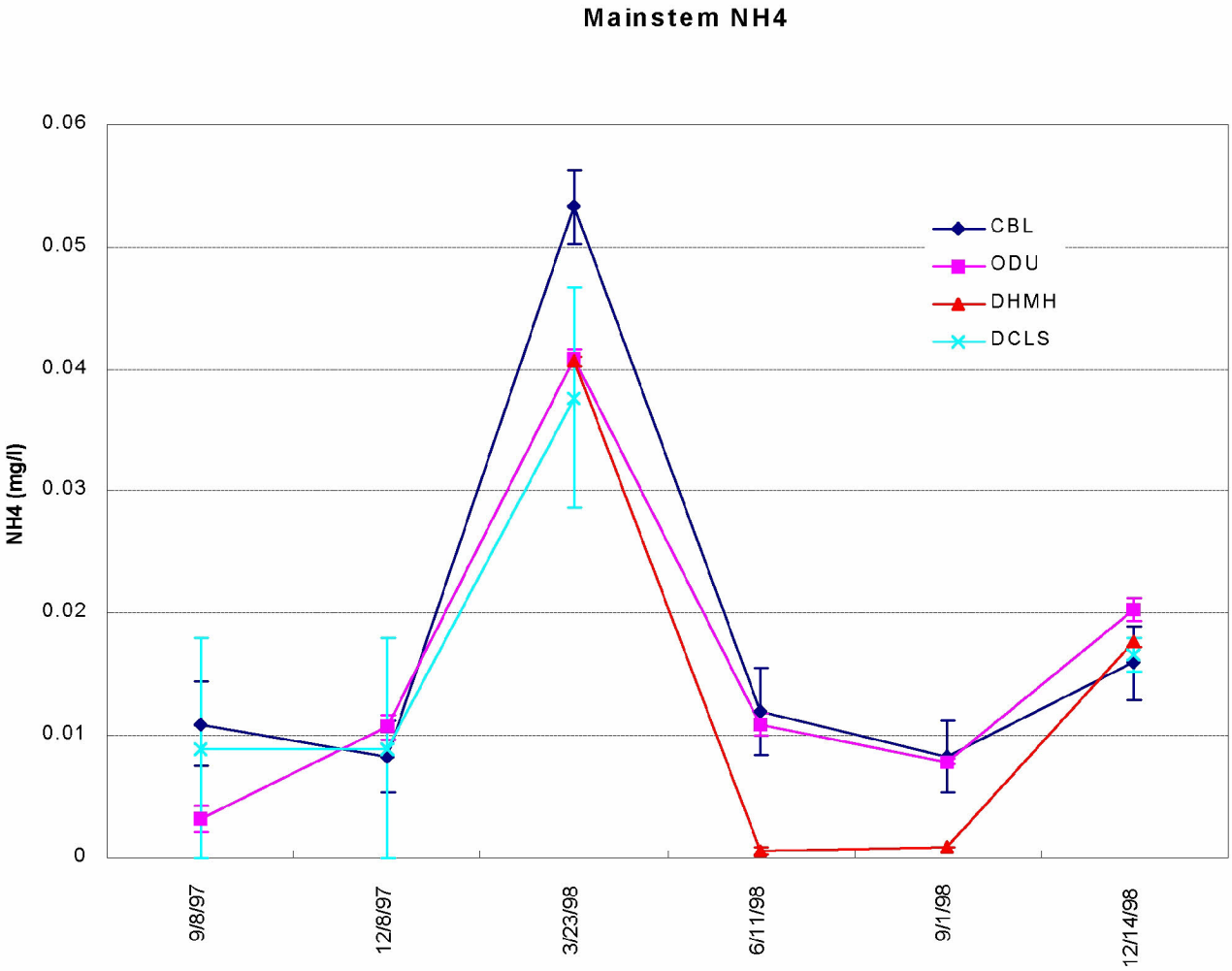
LS Means Results

Of Means	Of Residuals
CBL ODU DHMH DCLS	**DCLS CBL DHMH ODU**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



There were only two dates when data were available for all four labs therefore, the graphical analysis could not be performed.

Discussion

Although no bias was detected by the LS means analysis, after review of the graphical analysis it would appear that DHMH had several problems in their method, however they could not identify the source of the differences.

Parameter: Nitrate + Nitrite

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Nitrate + Nitrite Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F in field, triplicate polystyrene AA cups	Vacuum, 0.7μm GF/F in field HDPE	Vacuum 0.7μm GF/F in field, HDPE.	Vacuum, 0.7μm GF/F in field, HDPE
Glassware	Cleaned w/ 10% HCl, DI rinsed	Liquinox , w/ tap water rinse, rinsed twice w/ 4N IICl then 9 times w/ RG	Washed in 1:1 HCl, DI rinsed.	Haemo-sol, rinsed w/tap water, rinsed w/DI water.
Method	Automated cadmium reduction, EPA 353.2.	Automated cadmium reduction, EPA 353.2.	Automated cadmium reduction, EPA 353.2.	Automated cadmium reduction, EPA 353.2.
Instrumentation	Technicon AAII; 550 nm filter photometer, Cu/Cd column 50 mm flow cell	*1/94-12/95*: SIC continuous flow analyzer *1/96* on: Skalar SAN^{plus}, 540 nm, Cu/Cd column. Auto background/matrix correct w/ 1010nm filter,75mm flow cell	Skalar SAN^{plus}, 540 nm Cu/Cd column, auto background/ matrix correction w/ 620 nm filter, 50 mm flow cell	Alpkem model 3570 with SoftPac software, Cu/Cd column, 540 nm filter, 5 mm flowcell
Inst. Maintenance	Rinsed w 1N HCl for 15 min. after analysis, DI for 15 min.	Daily: Rinse w/ RGW for 15 min. Weekly: Clean cartridge w/ 1% hypochlorite (hr), RGW rinse (hr). Align flow cell.	Rinsed w/ DI water daily. Rinsed w/ 1N HCl weekly and 1% hypochlorite weekly	Rinse w/DI for 10min, rinse w/2% HCL 30 sec, rinse w/DI 20 min, run w/0.1NnaOH for 60 sec, rinse w/DI 20 min
Reagents	Color Reagent (sulfa-nilamide & N-1-naphth-ylethylenediamine di-hydrochloride) w Brij-35, NH_4Cl	Color Reagent (sulfanilamide & N-1-naphthylethylene-diamine di-hydrochloride) w Brij-35, NH_4Cl w EDTA	Color Reagent (sulfa-nilamide & N-1-naphth ylethylenediamine di-hydrochloride) w Brij-35, NH_4Cl	Color Reagent (sulfa-nilamide, N-1-naphth-ylethylenediamine di-hydrochloride),brij-35, NH4Cl

Standards	KNO_3 dried at 45 °C. $NaNO_2$, dried at 45 °C & preserved w $CHCl_3$. Stds. diluted with DI water	KNO_3 dried at 103 °C. $NaNO_2$, dried at 103 °C (each preserved w $CHCl_3$) Sds. diluted with ASW	KNO_3 dried at 105 °C. Prepared fresh daily in DI water	KNO dried at 110°, preserved w/$CHCl_3$, Stds diluted with DI water.
Cd column check	NO_3^- std ≥ 90% NO_2^- std	NO_3^- std ≥ 90% NO_2^- std	NO_3/NO_2 std. between 95 - 105%	NO_3-NO_2, 86- 114%
Calibration Ranges	0.005 - 1.40 mg/L	0.003 - 0.10 mg/L	0.010 - 0.4000 mg/L	0.02 - 2.0 mg/L
Calculated MDL	0.0002 mg/L	0.0002 - 0.0025 mg/L	0.004 mg/L	0.002 mg/L
Lowest Standard	0.005 mg/L	0.003 mg/L	0.010 mg/L	0.02 mg/L
Number of splits with > 25% CV among replicates.	4/20 (all > 50% CV)	1/19	0/15	1/17
Std Ref Material % recovery range	95-117	94-102	?	96-108
CSSP spike % recovery range	**1994-1998** Range – 99 - 115 Mean – 104.4 Median – 104 **1997.5-1998** Range – 100 – 110 Mean – 103 Median – 101.5	**1994-1998** Range – 94 – 107 Mean – 99.2 Median – 99 **1997.5-1998** Range – 94 – 99 Mean – 97 Median – 97	**1994-1998** Range – Mean – Median – **1997.5-1998** Range – Mean – Median –	**1994-1998** Range – 95 – 108 Mean – 102.7 Median – 102.5 **1997.5-1998** Range – 99 – 108 Mean – 104.5 Median – 105.5

Holding Time & Temperature	≤ 28 days at -20°C	4°C ~ 4 hrs., frozen at -20°C ≤ 28 days	4°C ~ 24 hrs, frozen at -20°C ≤ 28 days	4°C for 48 hrs.

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.4350
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0808

LS Means Results

Of Means

DCLS CBL DHMH ODU

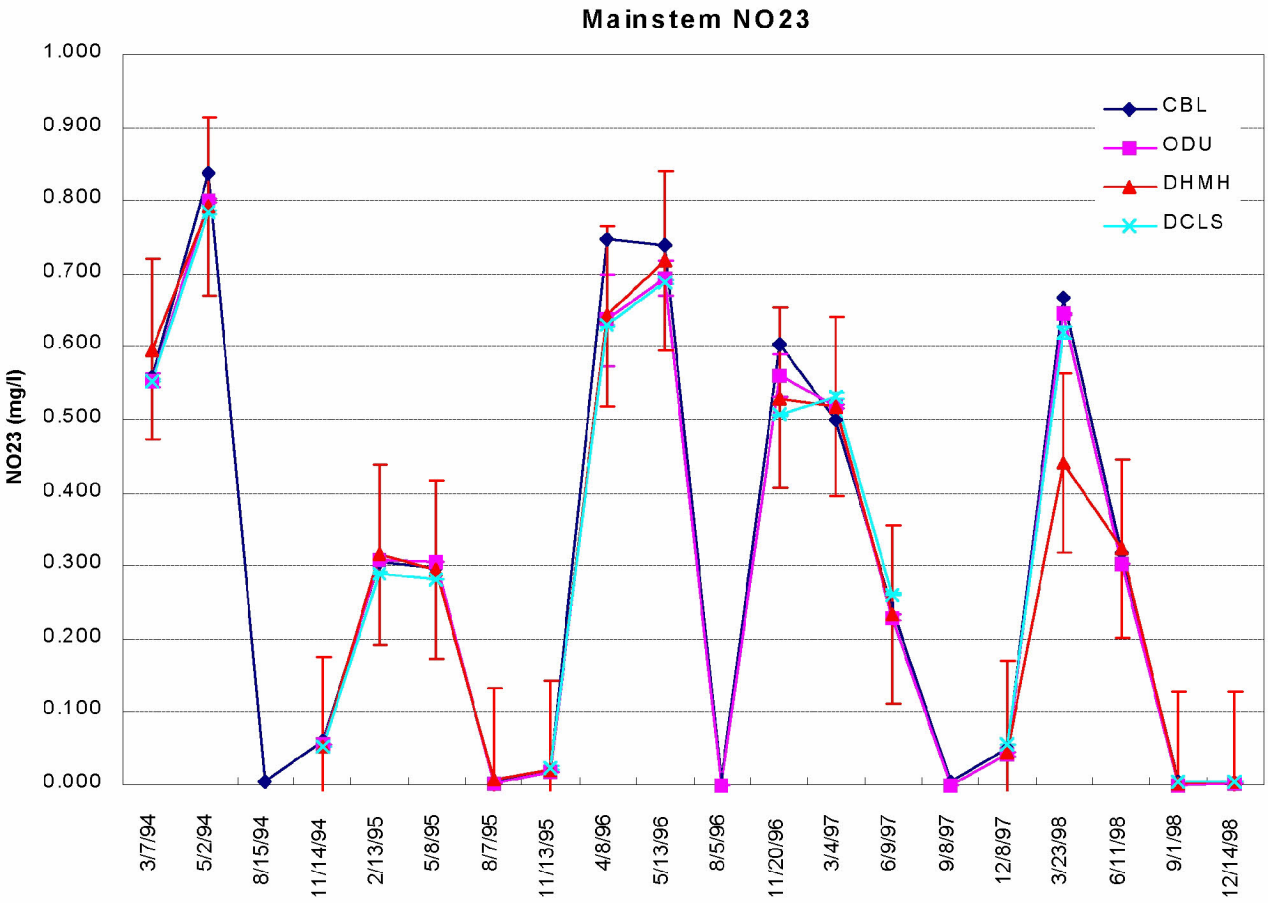
Of Residuals

DCLS DHMH CBL ODU

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



For the 15 dates for which data were available for all labs, CBL was different from ODU and DCLS more than 50% and ODU and DCLS were different from one another on more than 50% of the dates.

Discussion

Although differences were detected in the graphical analysis, it does not appear that there is an analysis problem. However, examination of the percent recovery data suggests that CBL and DHMH may have slight positive bias.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.1653
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0984

LS Means Results

Of Means

DCLS CBL DHMH ODU

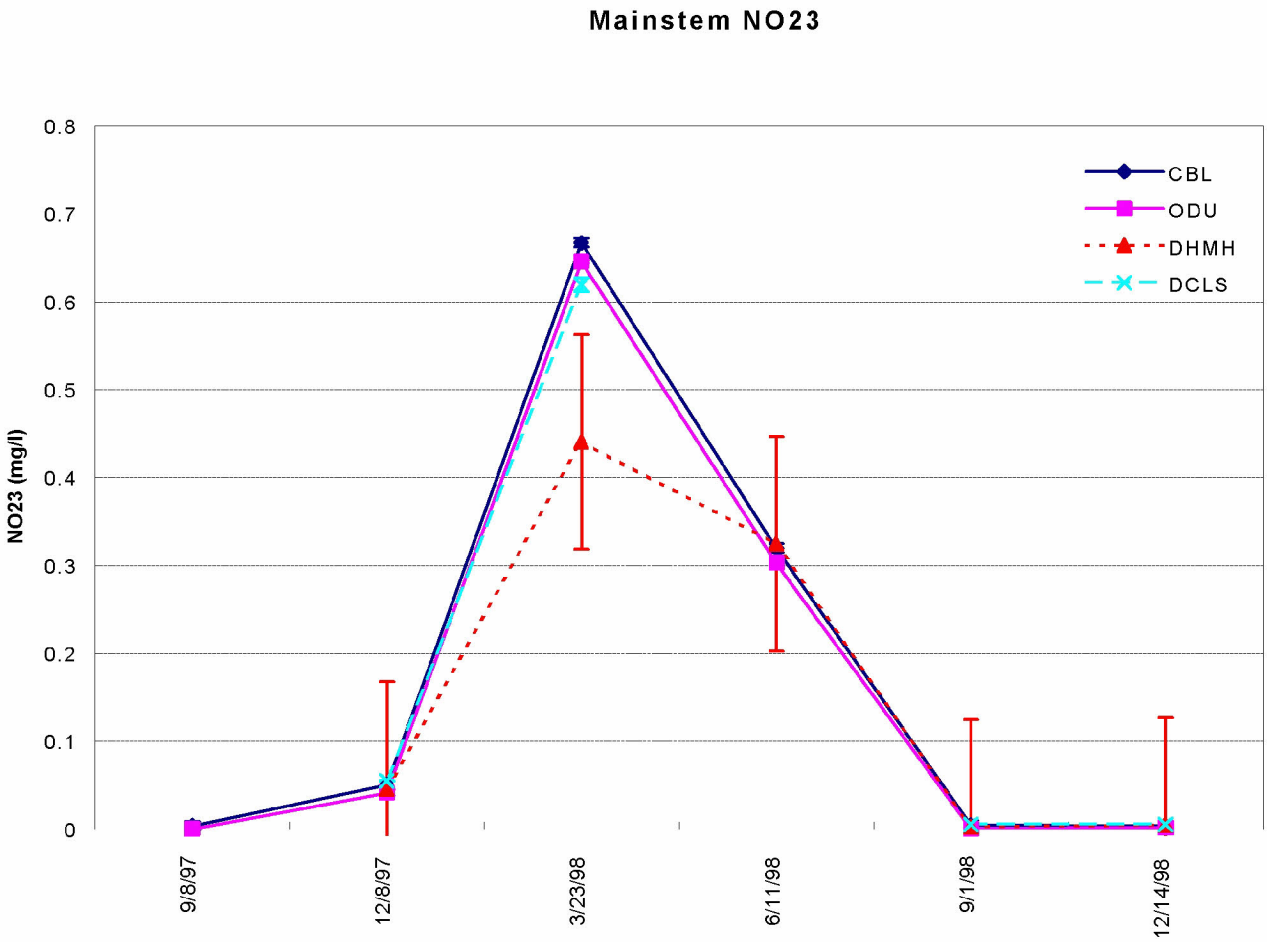
Of Residuals

DCLS DHMH CBL ODU

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the four dates where data were available for all labs, there were no pairwise comparisons where differences occurred on more than 50% percent of the four dates.

Discussion

There does not appear to be any analysis problems related to NO_{2+3}. However, examination of the percent recovery data suggests that CBL and DHMH may have slight positive bias.

Parameter: Nitrite

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Nitrite Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F in field, triplicate polystyrene AA cups	Vacuum, 0.7μm GF/F in field HDPE	Vacuum 0.7μm GF/F in field, HDPE.	Vacuum, 0.7μm GF/F in field, HDPE
Glassware	Cleaned w/ 10% HCl, DI rinsed	Liquinox , w/ tap water rinse, rinsed twice w 4N HCl then 9 times w/ RGW.	Washed in 1:1 HCl, DI rinsed.	Haemo-sol,w/tap water rinse, DI rinse.
Method	Automated colorimetric, diazotization, EPA 353.2.	*1/94-5/97:* Manual colorimet. diazotization, EPA 353.3. *6/97 on:* Auto. colorimetric, diazotization, EPA 353.2.	Automated, colori-metric, diazotization EPA 353.2.	Automated, colori-metric, diazotization EPA 353.2.
Instrumentation	TrAAcs-800; 520 nm filter photometer, 37 C heating bath 50 mm flow cell	*1/94-5/97*: spectrophotometer *6/97 on*: Skalar SAN^{plus}, 540 nm. Auto background/ matrix correct (620 nm filter) 75 mm flow cell	Skalar SAN^{plus}, 540nm. Auto background/ matrix correction w/ 620 nm filter. 50 mm flow cell	Alpkem model 3570 with SoftPac software. 540nm filter, 5 mm flow cell
Inst. Maintenance	Rinsed w 1N HCl for 15 min. after analysis, DI for 15 min.	Daily: Rinse w/ RGW for 30 min. Weekly: Clean cartridge w 1% hypochlorite (hr), RGW rinse (hr). Align flow cell.	Rinsed w/ DI water daily. Rinsed w/ 1N HCl weekly and 1% hypochlorite weekly	Rinse w/DI for 10 min, rinse w/ 2% HCl 30 sec, rinse w/DI 20 min, rinse w/0.1N NaOH 60 sec, rinse w/DI for 20 min.

Reagents	Separate color reagents: sulfanilamide, N-1-naphthylethylenediamine dihydrochloride w Brij-35	Combined color reagent: (sulfanilamide & N-1-naphthylethylene-diamine di-hydrochloride) w Brij-35	Combined color reagent: (sulfanilamide & N-1-naphthylethyl-enediamine dihydro-chloride) w Brij-35, DI water w Brij-35	Color Reagent (sulfa-nilamide, N-1-naphth-ylethylene-diamine di-hydrochloride), brij-35, NH_4Cl
Standards	$NaNO_2$, dried at 45 °C & preserved w $CHCl_3$ Stds. diluted with DI water.	$NaNO_2$, dried at 103 °C & preserved w $CHCl_3$. Standardize stock monthly. Stds. diluted with ASW.	$NaNO_2$, dried at 103 °C. Made fresh daily in DI water.	KNO_2 dried at 110°C, preserved w/$CHCL_3$, Stds diluted w/DI water.
Calibration Ranges	0.0028-0.042 mg/L	0.001-0.040 mg/L	0.010 - 0.100 mg/L	0.002 - 0.200 mg/L
Calculated MDL	0.0003 mg/L	0.0002-0.0010 mg/L	0.002 mg/L	0.02-0.002 mg/L
Lowest Standard	0.0028 mg/L	0.001 mg/L	0.010 mg/L	0.002 mg/L
Number of splits with > 25% CV among replicates.	3/20	1/20	0/16	1/20
Std Ref Material % recovery range	None	None	None	95-109
CSSP spike % recovery range	**1994-1998** Range – 96 – 105 Mean – 99.1 Median – 99 **1997.5-1998** Range – 98 – 102 Mean – 99.8 Median – 100	**1994-1998** Range – 95 – 108 Mean – 99.8 Median – 99 **1997.5-1998** Range – 98 – 100 Mean – 99.3 Median – 99.5	**1994-1998** Range – 70 – 114 Mean – 100.1 Median – 100 **1997.5-1998** Range – 70 – 105 Mean – 94.3 Median – 101	**1994-1998** Range – 98 – 108 Mean – 102 Median – 102 **1997.5-1998** Range – 98 – 102 Mean – 100.7 Median – 101

Holding Time & Temperature	≤ 28 days at -20°C	4°C ~ 4 hrs., frozen -20°C ≤ 28 days	4°C ~ 24 hrs, frozen at -20°C ≤ 28 days	4°C for 48 hrs.

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.4454
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0600

LS Means Results

Of Means

DHMH DCLS CBL ODU

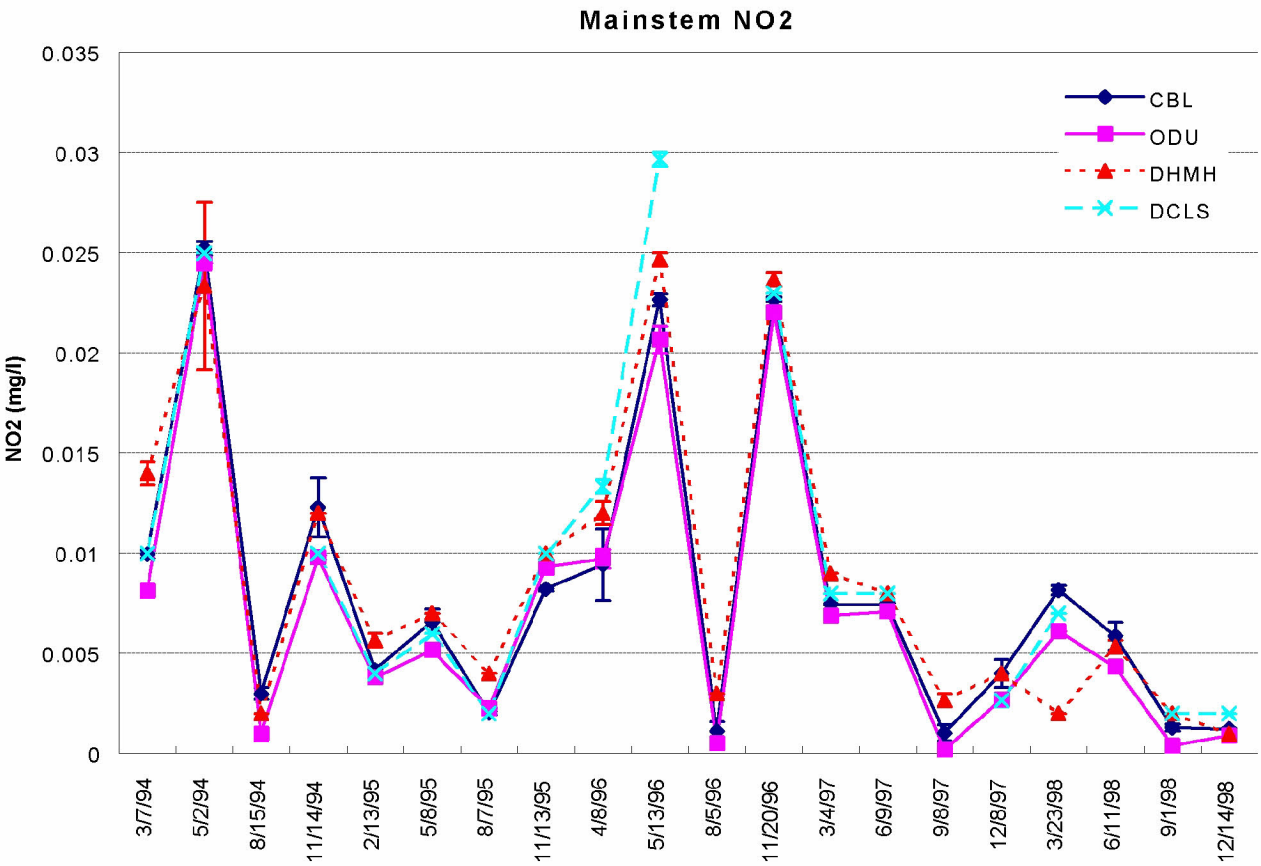
Of Residuals

DCLS ODU DHMH CBL

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the sixteen dates where there were data available for all four labs, all pairwise comparisons resulted in differences occurring in more than 50% of the dates.

Discussion

Although all labs failed the graphical analysis, it does not appear that an analytical problem with NO2 exists. Failure of the graphical analysis was apparently due to each labs small error bars.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.4758
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.4277

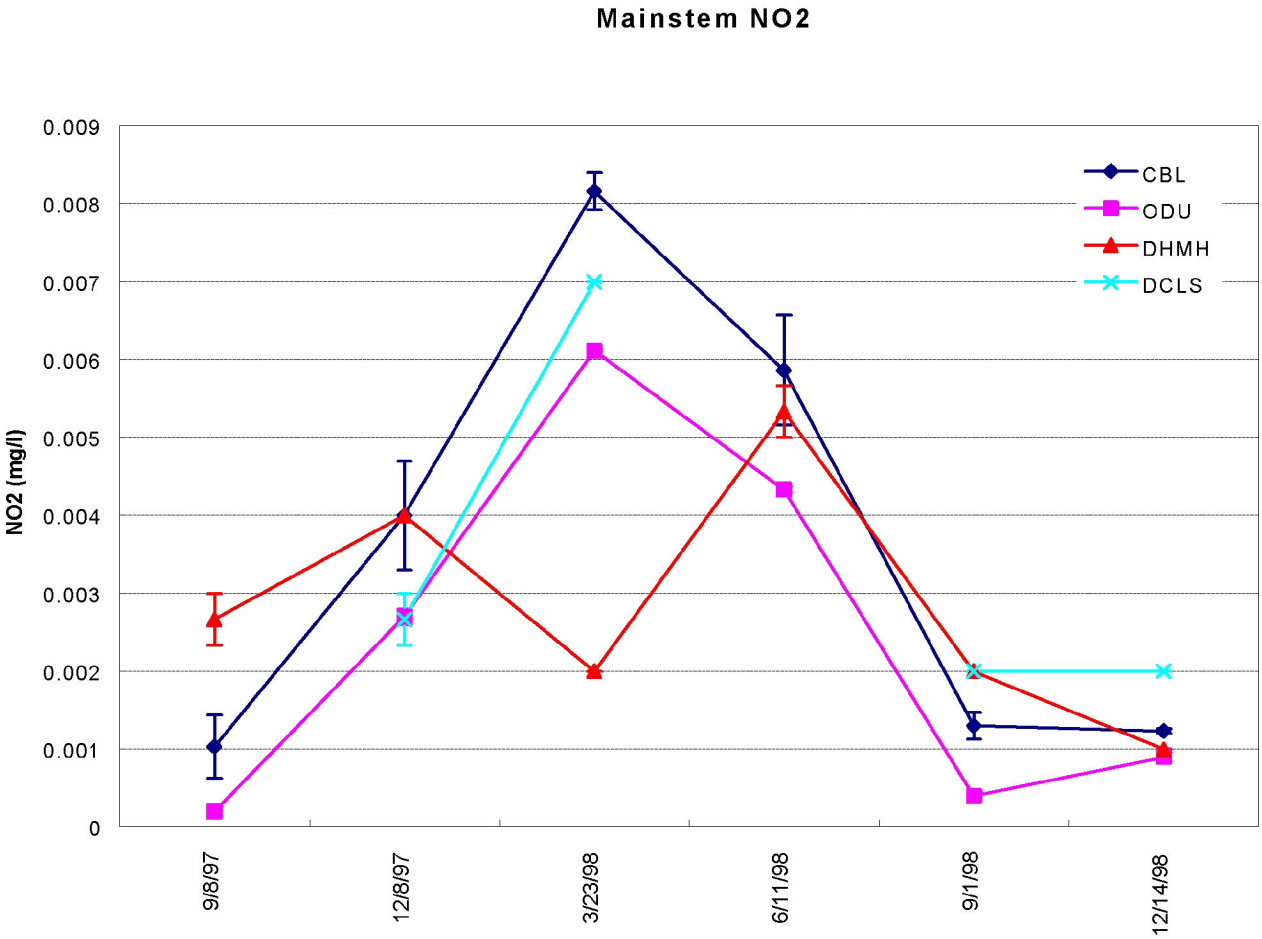
LS Means Results

Of Means	Of Residuals
DCLS CBL DHMH ODU	**DHMH ODU DCLS CBL**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Analysis



For the four dates where data for all labs were available, all labs failed the pairwise comparisons.

Discussion

Although all labs failed the graphical analysis, this was most likely due to small error bars and not indicative of a problem. More importantly, no labs were consistently higher or lower than one another (i.e. no bias) and, therefore, there do not appear to be any analysis issues with NO2.

Parameter: Total Suspended Solids

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): All labs measure directly

Total Suspended Solids Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	0.7μm GF/F filters dried 103-105 °C overnight, pre-weighed to 10^{-4} g. 250-500 mL sample are field vacuum filtered in duplicate, DI rinsed. Filters kept in Al pouchs.	0.7μm GF/F filters rinsed 3X RGW, dried at 103-105°C for ≥ 1 hr., pre-weighed to constant 10^{-4} g. 250-1000 mL sample are field vacuum filtered, RGW rinsed. Filters kept in plastic holders.	0.7 μm GF/F rinsed 3X w 20 mL DI, dried at 105°C for 30 min, muffled at 550°C for 15 min. Lab filters sufficient vol. to obtain 10 - 200 mg of residue.	1.5 μm GF/F rinsed 3X w 20 mL DI, dried at 103-105°C for ≥1 hr, pre-weighed to 10^{-4} g. Lab filters 50-250 mL sample, DI rinsed.
Glassware & Cleaning	100 & 250 mL plastic graduated cylinders, aluminum weighing pans.	500 mL & 1 L plastic grad-uated cylinders. Liquinox , w/ tap water rinse, rinsed 2X w/ 4N HCl then 9X w/ RGW.		100 mL plastic graduated cylinder
Method	Solids dried at 103-105 °C overnight, desiccated & weighed to 10^{-4} g. Some re-dried at 103 °C to constant wt (± 0.5mg). Duplicates averaged. Std. Meth. 2540D	Solids dried at 103-105 °C for ≥ 1 hr., desiccated & weighed to 10^{-4} g. All samples re-dried at 103 °C to constant wt. (± 0.5mg)		Solids dried at 103-105 °C for 1 hr, desiccated & weighed to 10^{-4} g. All samples re-desiccated to constant weight. (± 0.5 mg)
Analytical Balance Calibration	with auto data entry	Satorius series MC1, model RC 210 S Daily check w Class S 0.1 g Monthly check with range of Class S weights.	AT 261 Delta Range-Mettler AT 250 - Mettler.	Mettler Toledo model AG 204. Daily internal calibration check, Class S weights weekly.
Inst. Maintenance	Service check ___	Balances are serviced at least annually by a qualified service engineer. Class S weights re-certified annually		Balance serviced every two years by a qualified service engineer.

QC Samples	1 rep every 10 samples	1 field blank per 10 samples 1 replicate every 10 samples Quarterly SRM	1 rep every 10 samples	
Calculated MDL	2.4 mg/L	1.2 - 3.3 mg/L	3.0 mg/L	1.0 mg/L
Number of splits with > 25% CV among replicates.	0/20	1/18	5/20	2/7
Std Ref Material % recovery range	None	None	None	None
CSSP spike % recovery range	Not Applicable	Not Applicable	Not Applicable	Not Applicable
Holding Time & Temperature	≤ 28 days at -20°C	4°C ~ 4 hrs., frozen -20°C ≤ 28 days	4°C ≤ 7 days	4°C ≤ 7 days

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.2529
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0001

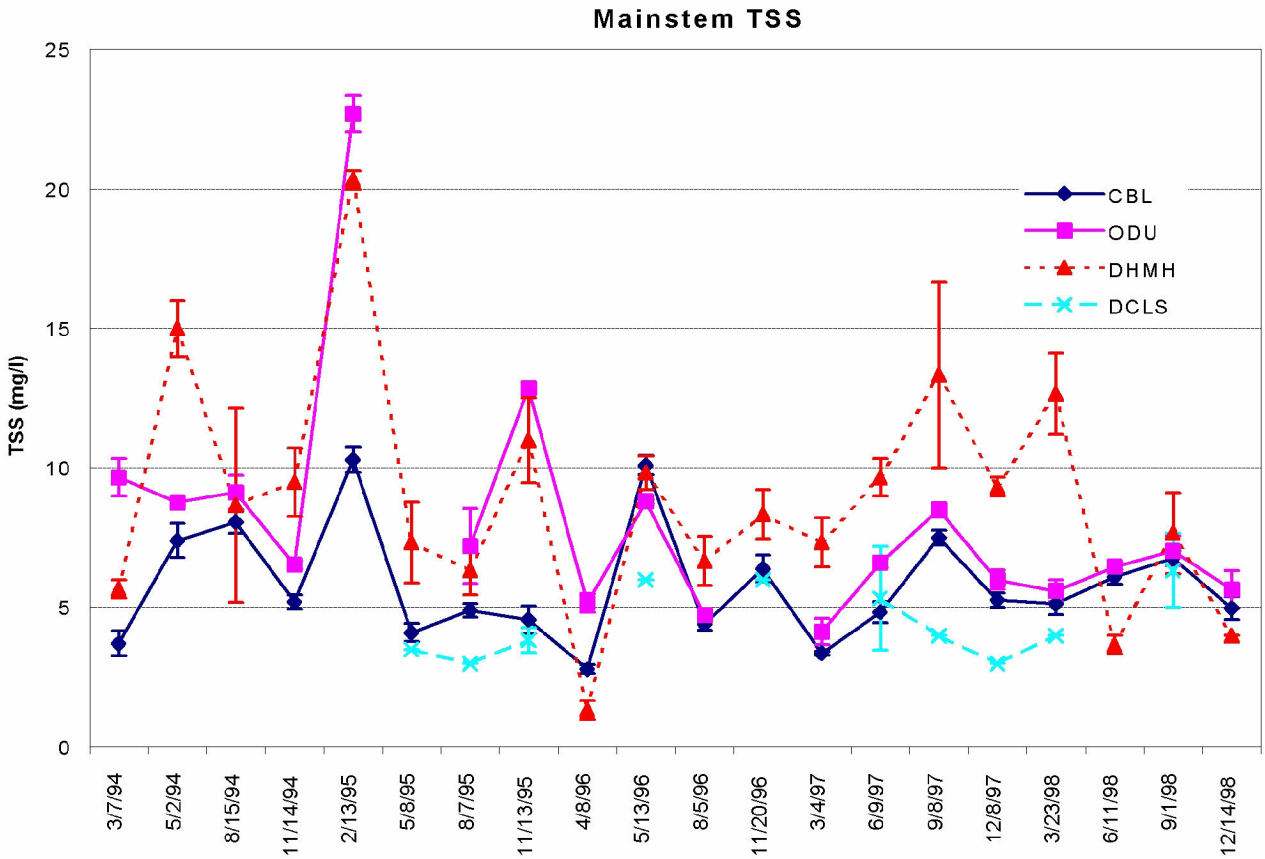
LS Means Results

Of Means	Of Residuals
DCLS CBL ODU DHMH	**CBL ODU DCLS DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data, which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DCLS was consistently different from all other labs and that CBL and DHMH were consistently different from one another. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Graphical analysis show that of the dates when data were available for all labs, only the pairwise comparisons between CBL and DCLS were not different in excess of 50% of the dates.

Discussion of Total Suspended Solids

It appears, from the results of the LSM, that DCLS has a negative bias and, relative to DCLS and CBL, DHMH has a positive bias. The graphical results also support this conclusion. The positive bias was probably due to DHMH not redrying TSS samples to a constant weight. Redrying was initiated in May 1998. The negative bias attributed to DCLS needs to be investigated.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.2192
Lab	0.0001
Date*Lab	0.0039
Lab using Date*Lab error term	0.0030

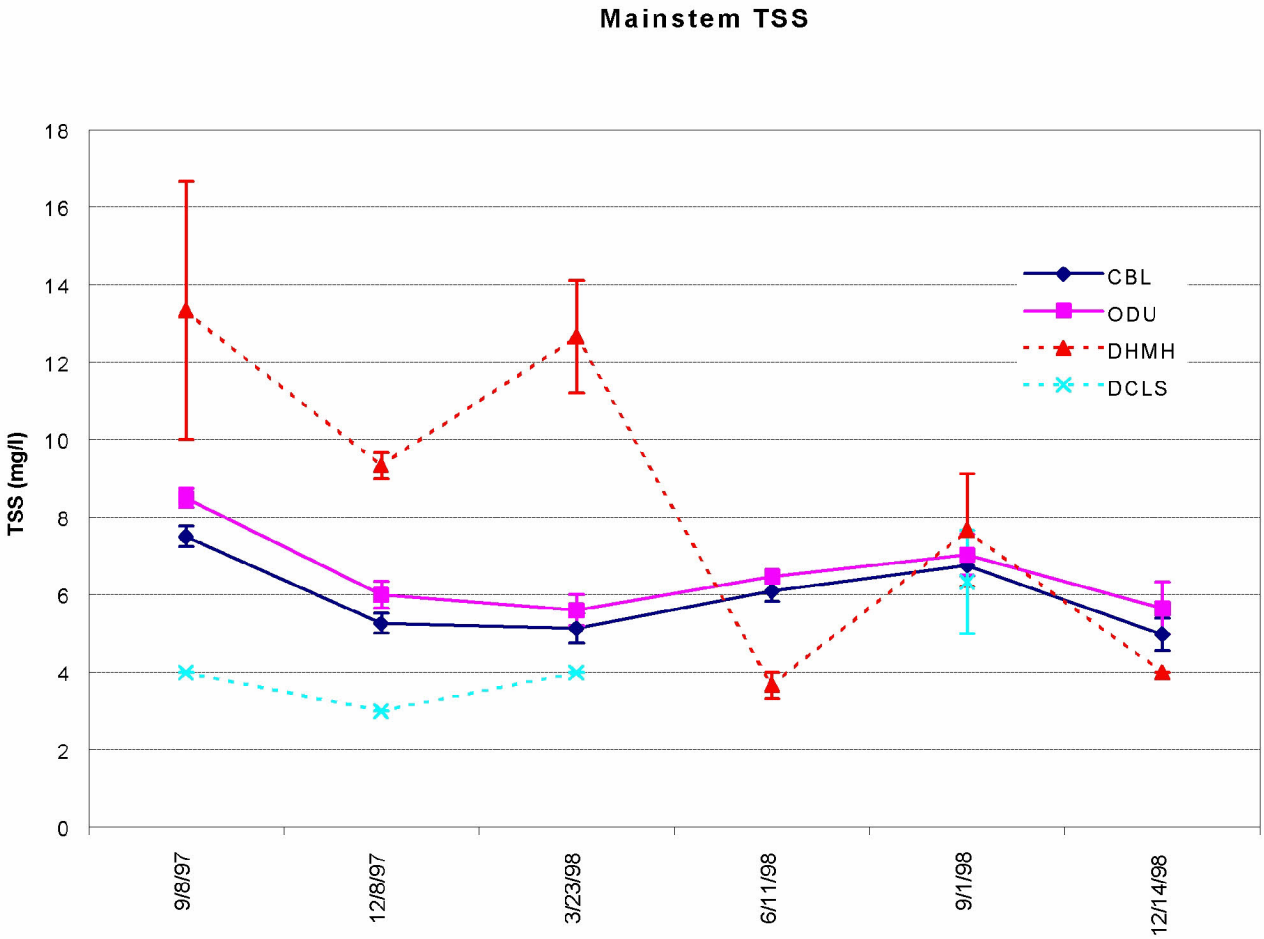
LS Means Results

Of Means	Of Residuals
DCLS CBL ODU DHMH	**CBL DCLS ODU DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DHMH was consistently different from all other labs and that ODU and DCLS were consistently different from one another. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the four dates when data was available for all labs, only the pairwise comparisons between CBL and ODU were not different on more than 50% of the dates.

Discussion

It appears, from the results of the LSM, that DCLS has a negative bias and, relative to DCLS and CBL, DHMH has a positive bias. The graphical results also support this conclusion. The positive bias was probably due to DHMH not redrying TSS samples to a constant weight. Redrying was initiated in May 1998. The negative bias attributed to DCLS needs to be investigated.

Parameter: Particulate Carbon

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL, ODU and DCLS measure directly, DHMH measures indirectly (TOC – DOC).

Particulate Carbon Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS (after 2/95)	DHMH
Sample Filtration & Preparation	1) 25 mm GF/F muffled at 550 °C for 90 min. 2) Particulates are field filtered in duplicate, placed in Al foil pouch. 3) Filters dried at 45 °C overnight.	1) Filters & glass vials are muffled at 550C for 15 min & 4 hrs respectively. 2) Particulates are field filtered (≤ 50 mL sample) on 13 mm GFF, placed in glass scintillation vials. 3) Filters dried at 50°C over-night, dessicated.. After 6/97, no chloroform/methanol cleaning of tin sample cups	1) Filter prep? 2) Particulates are field filtered (25-250 ml sample) on 25 mm GFF, 3) Filtlers dried over-night at 50°C Sample cup precombust at 875°C for 1 hr.	Calculated PC = TOC - DOC 0.5 L polyethylene cubitainer Std. Methods 5310B, Combustion Infrared
Method	Filters & Al capsule placed into nickel sleeves & combusted at 975°C. C_X O_X cmpds are reduced to CO_2(g).	Filters placed into tin sample cups are flash combusted at 1040°C. A series of catalytic and Cu reducing reactors convert C_X O_X cmpds to CO_2(g).	Combusted at 990°C	
Instrumentation	Exeter CE-440 Elemental Analyzer w Cu reduction column, He carrier gas & thermal conductivity detector.	Carlo Erba C/N gas chromat-ograph equipped with combustion & Cu reduction columns, He carrier gas & a thermal conductivity detector.	Exeter Model CE-440 Elemental Analyzer, Cu reduction column, He carrier gas & thermal conductivity detector.	
Inst. Maintenance	Columns renewed after 300-600 samples	Both columns renewed after 300-600 samples		

Reagents	Helium carrier gas	Helium carrier gas		
Standards	1.5 mg acetanilide (71.09%N)	Chloramine-T dried at 50°C for 30 min.	Acetanilide	
Calibration Ranges	None: standards run as recovery check.	0.05 mg - 1.0 mg 5 pt. calibration curve	None: standards run as recovery check.	
Calculated MDL	0.0759 mg/L	0.0615 - 0.196 mg/L	0.1 mg/L	1.0 mg/L (0.5 + 0.5)
Lowest Standard	None	0.05 mg	None	Not applicable
Number of splits with > 25% CV among replicates.	0/20 (all < 6.3% CV)	1/18	7/11	3/12
Std Ref Material % rec. range	None	None	None	91-105 (TOC)
CSSP spike % recovery	None	None	None	68-129 (DOC)
Holding Time & Temperature	≤ 28 days at -20°C	≤ 28 days at -20°C	≤ 28 days at -20°C	4°C≤ 48hrs.

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.3164
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0006

LS Means Results

Of Means

DCLS DHMH ODU CBL

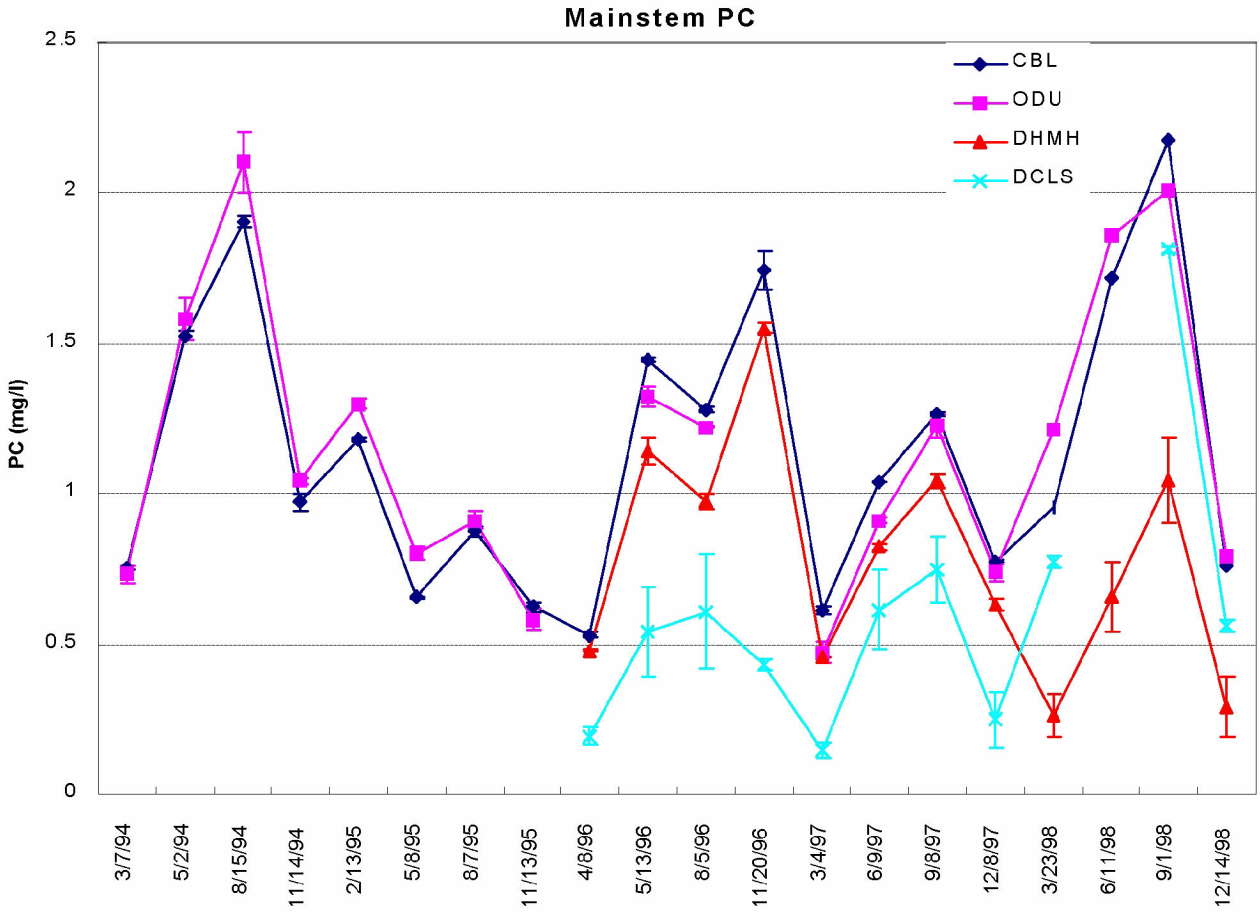
Of Residuals

CBL ODU DCLS DHMH

The ANOVA results indicate that there is no replicate affect on variability within the data, which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that DCLS and DHMH were consistently different from ODU and CBL. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Graphical analysis shows that of the nine dates when there were data available for all labs, all labs failed the pairwise comparisons.

Discussion of Particulate Carbon

It appears that DCLS has a negative bias and since mid 1997 DHMH has developed a negative bias. DCLS also had a negative bias in the particulate nitrogen method that is analyzed simultaneously. This needs to be investigated.

DHMH reviewed their TOC and DOC methods in December 1998 and found the cause of high DOC results and subsequent low PC results. Further improvements to their method will be implemented in 1999.

The difference detected between CBL and ODU in the graphical analysis is apparently due to both labs small error bars for this parameter.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.6652
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.0269

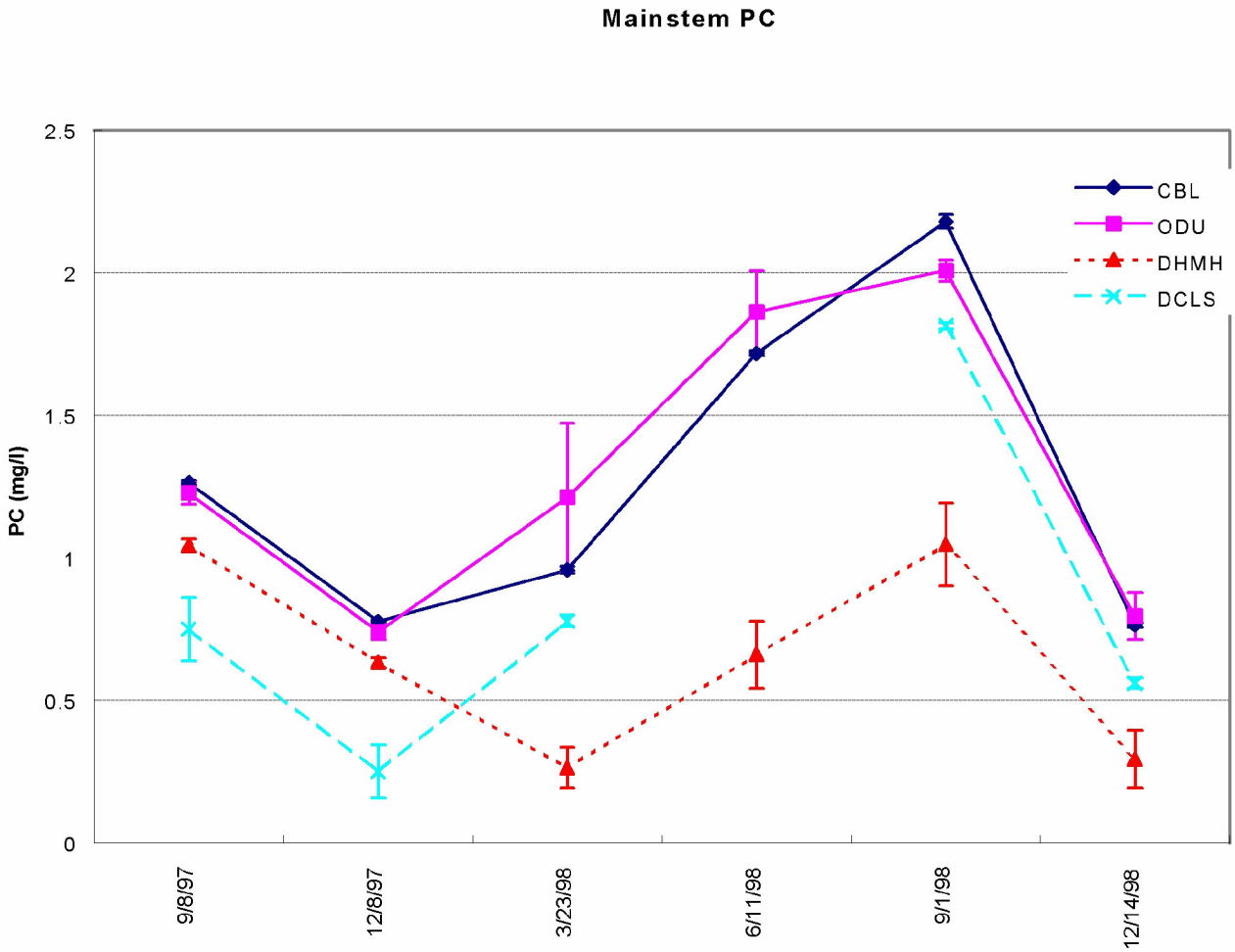
LS Means Results

Of Means	Of Residuals
DHMH DCLS CBL ODU	**CBL ODU DCLS DHMH**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, and that this difference was greater than the within run variability associated with each lab.

The LS means results indicate that there were no consistent differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the five dates for which data were available for all labs, all labs were different from one another on more than 50% of the dates except CBL and ODU.

Discussion

Although the LSM analysis did not detect any significant differences in the 97.5 – 98 data, looking at the graph of the data, it does appear that both DCLS and DHMH have a negative bias.

Parameter: Silica

Labs: CBL, ODU, DCLS and DHMH

Measurement (direct/indirect): CBL, ODU and DHMH measure directly, DCLS measures SiO2 (Si = (SiO2/2.14))

Silica Method Comparison - Mainstem Labs

Variable	CBL	ODU	DCLS	DHMH
Sample Filtration & Container	Vacuum, 0.7μm GF/F in field, triplicate polystyrene AA cups.	Vacuum, 0.7μm GF/F in field 125 mL HDPE. (TSS filter preparation.)	Vacuum 0.7μm GF/F in field, HDPE.	Vacuum, 0.7μm GF/F in field, HDPE
Glassware	Low silica glassware Cleaned w/ 10% HCl, DI rinsed	All plastic, except pipets. Liquinox , w/ tap water rinse, rinsed twice w/ 4N HCl then 9 times w/ RGW.	Plastic/Nalgene used wherever possible. Washed in 1:1 HCl, rinsed with DI water.	Hemo-Sol & demineralized H_2O. Plastic is used wherever possible.
Method	EPA 366.0 Automated molybdenum blue method. Blue color is formed by the reduction of silicomolybdate and ascorbic acid in acidic conditions. Oxalic acid elim. $PO_4^{=}$ interference.	EPA 366.0 Automated molybdenum blue method. Blue color is formed by the reduction of silicomolybdate and ascorbic acid in acidic conditions. Oxalic acid eliminates $PO_4^{=}$ interference.	EPA 370.1 Automated molybdate/ascorbic acid. Blue color formed by silico-molybdate + ascorbic acid in acidic cond. Oxalic acid elim. $PO_4^{=}$ interference.	EPA 370.1 Automated molybdate/ascorbic acid. Blue color formed by silico-molybdate + ascorbic acid in acidic cond. Oxalic acid elim. $PO_4^{=}$ interference.
Instrumentation	Technicon TrAAcs-800; 800 nm filter photometer 37°C Heating Bath 50 mm flow cell	*1/94-12/95*: SIC continuous flow analzer 1/96 on: Skalar SAN^{plus}, 810nm w auto background/ matrix correct (1010nm filter) 75 mm flow cell	Technicon AA II 660 nm with 15 mm flow cell	Technicon AA II w 15 mm x 2.0 mm flowcell
Inst. Maintenance	Rinsed w/ DI and SDS for 10 min. after analysis	Rinsed w/ RGW for 30 min. after analysis. 1/wk: Cartridge cleaned w/ 0.5 N NaOH for hr., RGW for hr., flow cell aligned.	Rinsed w/ DI water daily. Rinsed w/ 0.5 N NaOH for hr. weekly	Rinsed w/DI for 30-45 min. after analysis

Reagents	Oxalic, H_2SO_4, ascorbic acids, ammon.molybdate. Isopropanol baseline sol n, NaOH wash water. SDS in H_2SO_4	Oxalic, H_2SO_4 & ascorbic acids, ammon. molybdate. ASW wash water. FFD6 in H_2SO_4 & ascorbic acid	Oxalic, H_2SO_4 & ascorbic acids, ammon. molybdate. DI water wash steol wetting agent	Oxalic acid, H_2SO_4, ascorbic acid, ammonium molybdate.
Standards & blanks	Na_2SiF_6 dried @ 45°C in DI H_2O	Sodium metasilicate nona-hydrate (Na_2SiO_3 - $9H_2O$) in ASW matrix water.	Na_2SiO_3 - $9H_2O$ in DI H_2O	Sodium Silicate (Fisher)
Calibration Ranges	0.281 - 2.10 mg/L	0.023 - 1.169 mg/L	0.1 - 10.0 mg/L	1 - 5 mg/L
Calculated MDL	0.01 mg/L	0.0000 - 0.0013 mg/L	0.1 mg/L	0.000- 0.10 mg/L
Lowest Standard	0.281 mg/L	0.002 mg/L	0.1 mg/L	1 mg/L
Number of splits with > 25% CV among replicates.	1/20	1/19	11/19	0/18
Std Ref Material % recovery range	None	None	84-112	100-105
CSSP spike % recovery range	**1994-1998** Range – 91 – 97 Mean – 93.9 Median – 93.5 **1997.5-1998** Range – 91 – 96 Mean – 93.5 Median – 94	**1994-1998** Range – 81-109 Mean – 98.4 Median – 99 **1997.5-1998** Range – 88 – 103 Mean – 95 Median – 95.5	**1994-1998** Range – 93 – 102 Mean – 99.5 Median – 100 **1997.5-1998** Range – 93 – 101 Mean – 98.3 Median – 99.5	**1994-1998** Range – 90 – 101 Mean – 95.7 Median – 95 **1997.5-1998** Range – 91 – 100 Mean – 96.8 Median – 97.5

Holding Time & Temperature	≤ 28 days at 4°C	≤ 28 days at 4°C	≤ 28 days at 4°C	≤ 28 days at 4°C

Split Results:
1994-1998

ANOVA results

Effect	*P Value*
Rep	0.1553
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.1256

LS Means Results

Of Means

CBL ODU DCLS DHMH

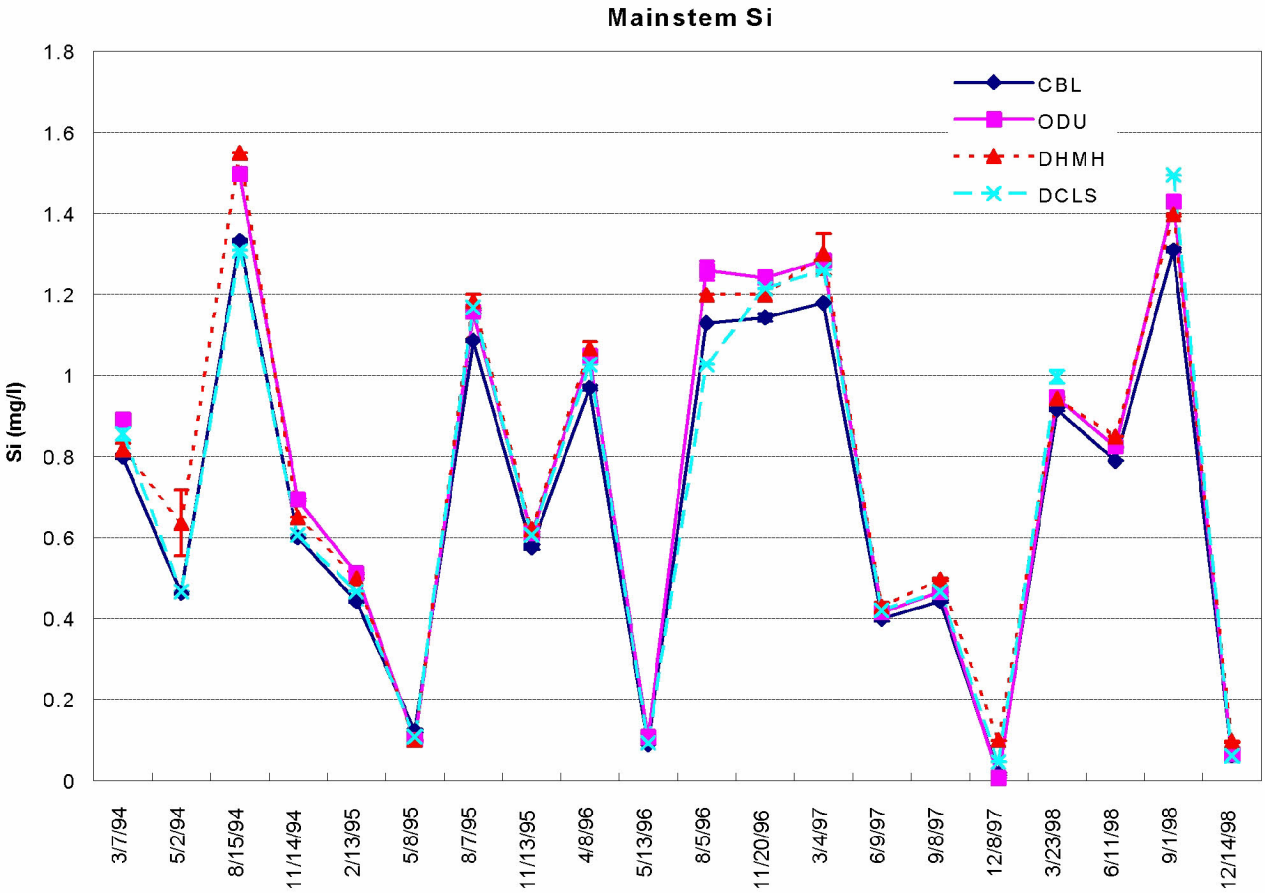
Of Residuals

DHMH ODU CBL DCLS

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results



Of the seventeen dates for which data were available for all labs, all labs failed the pairwise comparisons.

Discussion

The does not appear to be an analysis issue with Si. The failure of all labs in the graphical analysis is due to the small error bars. The spike recovery data indicates that CBL may have a negative bias with this parameter.

1997.5-1998

ANOVA results

Effect	*P Value*
Rep	0.3675
Lab	0.0001
Date*Lab	0.0001
Lab using Date*Lab error term	0.2181

LS Means Results

Of Means	Of Residuals
DHMH DCLS CBL ODU	**DHMH ODU DCLS CBL**

The ANOVA results indicate that there is no replicate affect on variability within the data which would indicate that the splitting procedure was conducted properly. The results also indicate that there was a difference among labs, that this difference varied through time, but that this difference was not greater than the within run variability associated with each lab.

The LS means results indicate that there were no differences among labs. The LS Means of the residuals indicate that, in terms of variability around the mean, there were no differences among labs.

Graphical Results

Of the five dates when data were available for all labs, all pairwise comparisons among labs failed.

Discussion

There do not appear to be any analysis problems related to Si. The failure of all labs in the graphical analysis is due to the small error bars. The Spike recovery data indicates that CBL may have a negative bias with this parameter.

Parameter: Chlorophyll

Labs: CBL, ODU, DCLS and DHMH

Measurement (Spectrophotometric/fluorometric): ODU, DCLS and DHMH measure spectrophotometrically; CBL measures fluorometrically.

Chlorophyll Method Comparison- Mainstem Lab

Variable	CBL (Fluorometric)	ODU	DCLS	DHMH
Field Procedures	NA	Samples collected in 1L brown HDPE bottles. Each bottle is sample rinsed (3x). $MgCO_3$ is immediately added (1ml per 1L sample). Filter pad moistened w/ DI. Grad. cyl. Rinsed 3x with DI and 2x with sample after inverting sample 20x. Sample inverted again. Vac 12 psi. Filtration time limited to 5 min. and generally only 300-500 mls of water filtered, depending on water turbidity. Filter folded in half and placed in foil and frozen immediately or placed on ice and frozen ASAP. Field Filtered.	Samples received day after collection at 4° C in opaque bottles w/ $MgCO_3$ added. Sample filtered immediately in semi darkness @ <2.9 psi. Amount filtered determined by color of filter and turbidity of water. Filter folded, stored in glass tubes and frozen until extraction (next day at the latest) Lab Filtered.	Samples collected in sample rinsed plastic containers. Container is vigorously shaken prior to filtration and graduate cylinder is sample rinsed. Sufficient vol. (100-1500 ml) is filtered to solidly color the filter pad. Vac. pressure <4.9 psi To the last 25 ml filtered, ~1 ml of concentrated $MgCO_3$ is added. Filter pad is folded in half and placed in foil pouch and stored on ice until they reach the field office where they are frozen. Field Filtered.
750 nm Interference Recentrifuge or Filter	Not applicable	If 750 nm absorbance >0.007, re-centrifuged for 5 min at 2300 rpm	If 750 nm absorbance >0.005 AU, sample filtered through glass fiber syringe filter	If the 750 nm absorbance is >0.005, re-centrifuged.

Grinding Techniques	Filter pad is briefly thawed, placed in a 15 mL glass centrifuge tube. 10 mL 90% acetone is added, pad is ground against the side of the tube using a pestle.	Pad placed in grinding tube, 3-4 ml 90% acetone added, pad ground at ~500 rpm with a tissue homogenizer. A TFE-fluorocarbon to glass pestle is used to fully macerate pad and cells	Pad placed into Pyrex tube. 2.0 ml aqueous acetone added to tubes and filter is ground for 1 min w/ Teflon pestle @500 rpm. 8.0 ml aqueous acetone used to rinse pestle into tube. Tubes capped and shaken and placed in chilled ultrasonic bath for 5 min. Tubes are mixed for 10 sec in vortex mixer, placed in light proof box and frozen until analysis	Filter pads removed from freezer and allowed to warm for 10 min. Pad placed in tissue grinder, 2-3 ml 90% acetone added. Sample ground for 2-3 min until homogenous, quant. transfer to cent. tube w/ acetone, transfer rinses to cent. tube, add acetone until vol is 15 ml. Capped tubes store in freezer.
Acidification	3-4 drops 5%HCl. Final Normality = 0.018-0.022	2 drops 1N HCl; wait 1 min but no longer than two to take final reading. Final Normality = 0.02	150 µl 0.1 N HCl, mixed w/ thin tube disp. pipette, 90 s wait. Final Normality = 0.03	3 drops 1N HCL, inverted to mix, 90 s. wait. Final Normality = 0.011
Acetone	Baker Analyzed ACS Reagent Grade (98.8% Acetone) diluted to 90% with water.	Baker Analyzed HPLC solvent (99.7%) diluted to 90% with ultrapure water. 5 drops 1N sodium bicarb added per liter.	Fisher OPTIMA grade (HPLC/Spec and Gas Chrom grade); 100 ml DI and enough acetone to make 1000 ml solution	Spectranalyzed acetone and certified ACS Sodium bicarbonate. 90% solution prepared by adding 40 ml DI to 3600 ml acetone. Solution buffered w/ 2ml 1N sodium bicarb.
Tubes	15 mL glass centrifuge tubes	glass	16X150 Pyrex, washed then rinsed w/ acetone	polypropylene, 15 ml, screw cap, acetone resistant
Ground & Extracted Samples	refrigerated overnight	overnight at 4 ° C; or frozen @ -20 to -70 ° C until analysis	frozen up to 1 week	frozen
Filter Type	Whatman GFF, 47mm, 0.7 µm	4.25 cm Whatman GF/F 0.7 µm	47 mm Whatman GF/F 0.7 µm	Whatman GFF, 47mm, 0.7 µm
Cell Size	NA	1.0 cm	2.0 cm	5 cm
Extract Volume Measure-ment	Known volume of acetone added.	Subtract filter/sediment plug volume from total volume in centrifuge tube.	Record exact amount of acetone added for grinding and extraction.	14mL - Bring acetone volume up to 15 mL, subtract 1 mL to account for volume of filter.
Spectropho-tometer	Sequoia Turner Fluorometer Model 112; Turner Designs Model TD700	Perkin-Elmer Model 559A dual beam spec 1.0nm band pass	Varian MS-200 @ 2.0 nm bandwidth	DU-65 Beckman; Bandwidth resolution is 2 nm from 200-600nm

Spectrophotometer Maintenance Schedule		monthly verification of wavelength accuracy using NIST SRM (holium oxide) filters. Periodic evaluation of slopes of calibration curves.	Major parameters of instrument performance checked monthly. Absorbance verified weekly	Light bulb replaced as needed. Manufacturer called for major problems
Calculation	Fluorometric	Ca = Chlorophyll corrected for Pheophytin (µg/l=[26.7(abs664nm-abs665nm)]xtvol(ml) / samp vol L abs664 = optical density before acidification abs665 = optical density after aciiication xtvol = extract volume samp vol = sample volume	Chla(mg/m3)=26.7(OD664b - OD665a)xV1 / V2xL where: OD665a = optical density after acid OD664b= optical density before acid V1 = volume of extract, L V2 = volume of sample, m3	Chla(mg/m3)= 26.7(OD664b -OD665a)xV1 / V2xL where: OD665a = optical density after acid OD664b= optical density before acid V1 = volume of extract, L V2 = volume of sample, m3 L = light path length??
Centrifuge Details	5 min at 1760 rpms, rinse down tubes, then centrifuge again	20 min at 2300rpm at 4° C	~500G for 20 min @ room temp	1st time - after extraction - 30min 3000 rpm 2nd time - before analyzing15 min 3000 rpm
Light Conditions	no light in hood where analysis is conducted but regular lighting in lab. Keep extracted samples in a box.	Lights are not dimmed, samples are kept in a cooler on ice	Subdued light; light proof box in freezer.	Subdued light in work area, no direct light exposure, samples covered w/ aluminum foil

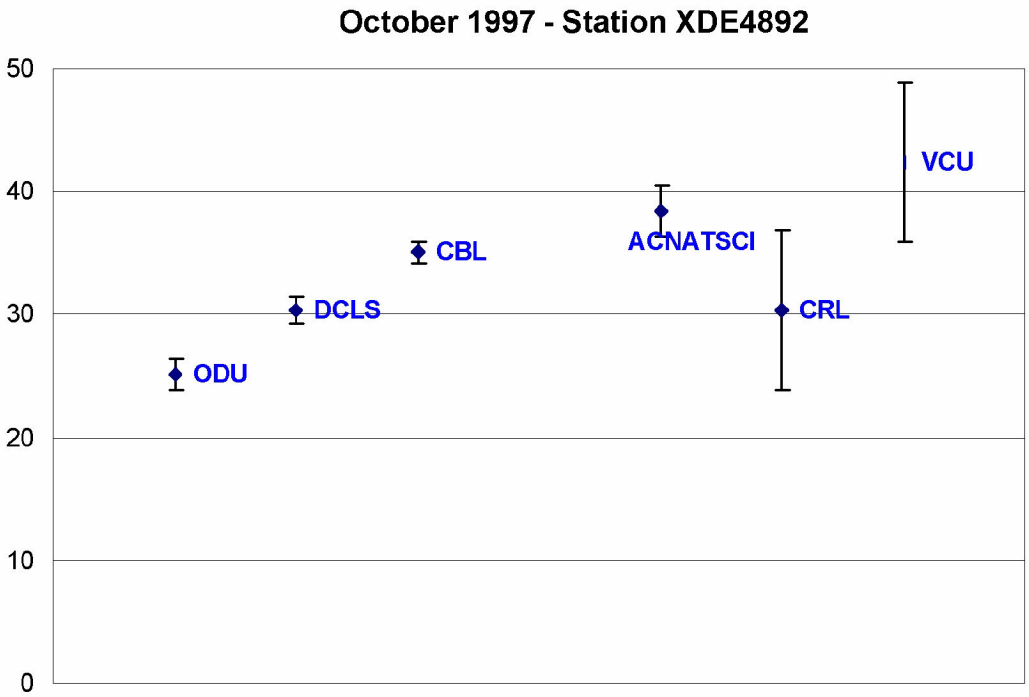
A Note on Chlorophyll

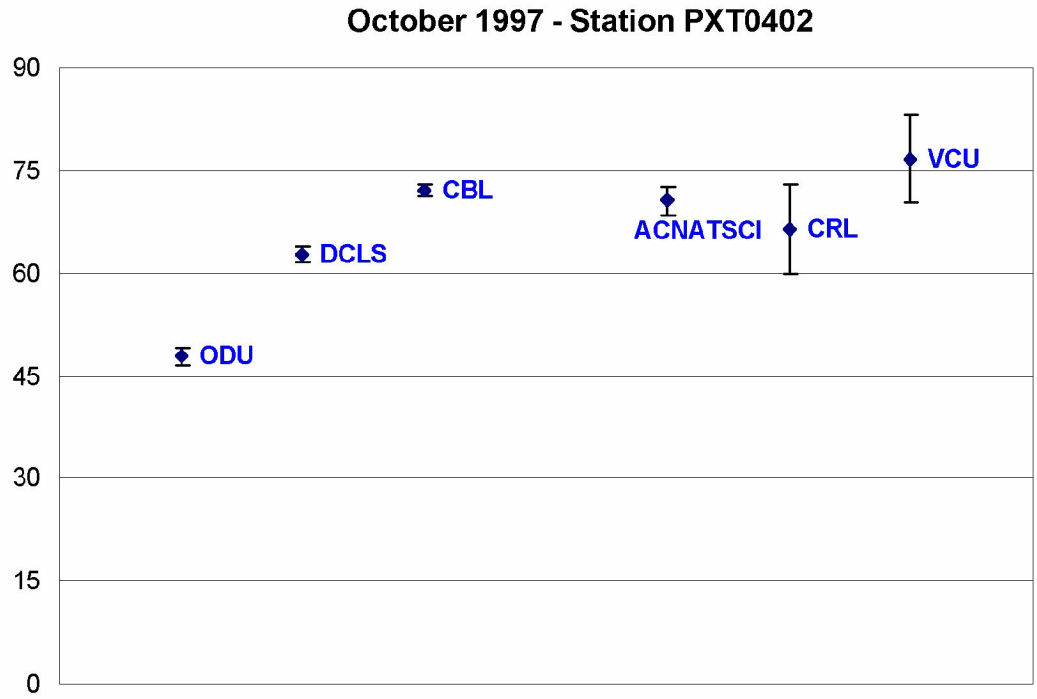
In the 1994-1998 period, chlorophyll was not measured by enough of the labs participating in the mainstem split to conduct a split sample analysis. In 1997, a disparity was observed between the chlorophyll values measured by the Maryland Department of Health and Mental Hygiene MDMH) and the Academy of Natural Sciences (ACNATSCI). The Academy conducts in vivo fluorescence monitoring in the mainstem of the Chesapeake Bay. As part of the calibration procedure, they collect water samples to measure chlorophyll spectrophotometrically. These calibration samples are drawn at the same time as are the samples which are sent to DHMH for analysis in the water quality monitoring program. Because the two labs were getting different chlorophyll results for water samples taken at the same time, the matter was brought to the attention of the Analytical Methods and Quality Assurance Workgroup.

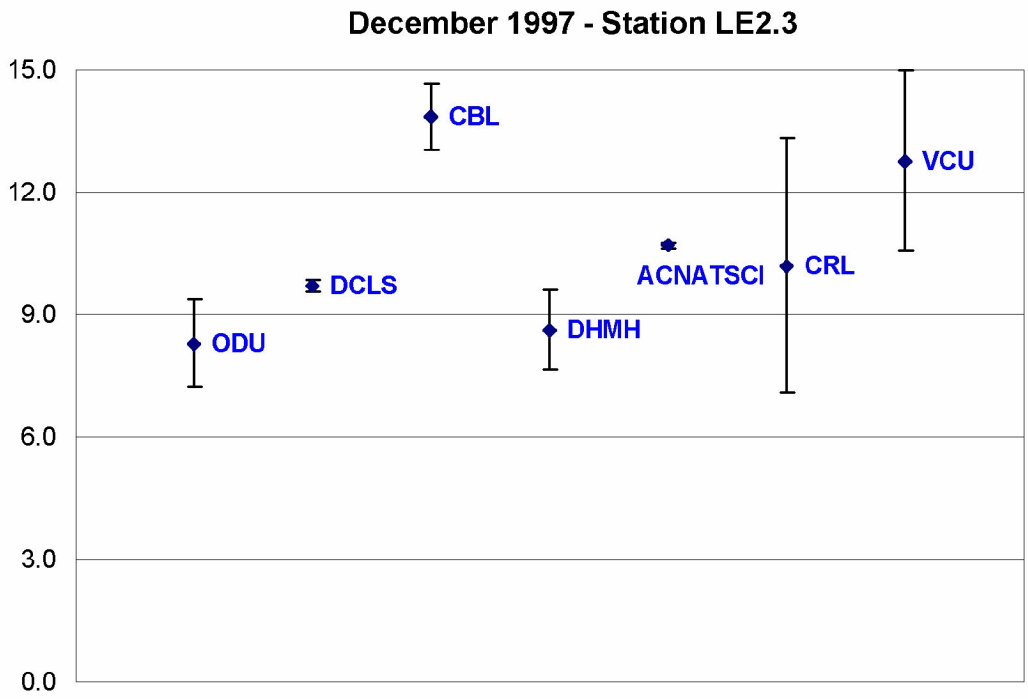
AMQAW requested that three splits be conducted. Seven labs (CBL, ODU, DHMH, DCLS, ACNATSCI, VCU [Virginia Commonwealth University], and CRL [EPA Central Regional Lab]) participated in October and December of 1997 and in May of 1998. Due to a lab accident, DHMH's results for the October split were not used and no results were obtained from CRL in the May Split). The October split consisted of 5 replicates each from two stations in the Patuxent (XDE4892 and PXT0402). The December split consisted of 5 replicates from station LE2.3 at the mouth of the Potomac. The May Split was prepared by the Chesapeake Biological Laboratory and consisted of 10 reps each of a low level natural and a high level cultured sample. The results of each of these splits are displayed graphically below. No consistent differences were detected between labs for any of the splits. All labs participating agreed that chlorophyll is

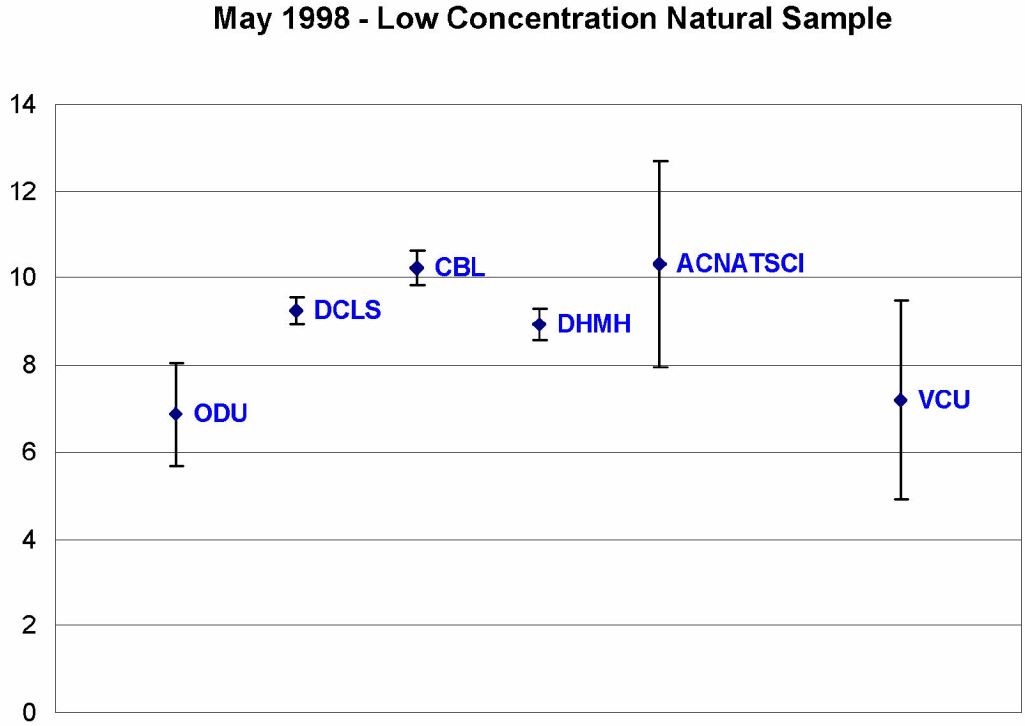
a highly variable parameter by nature and that the most benefit would be gained by focusing their efforts on using consistent methods.

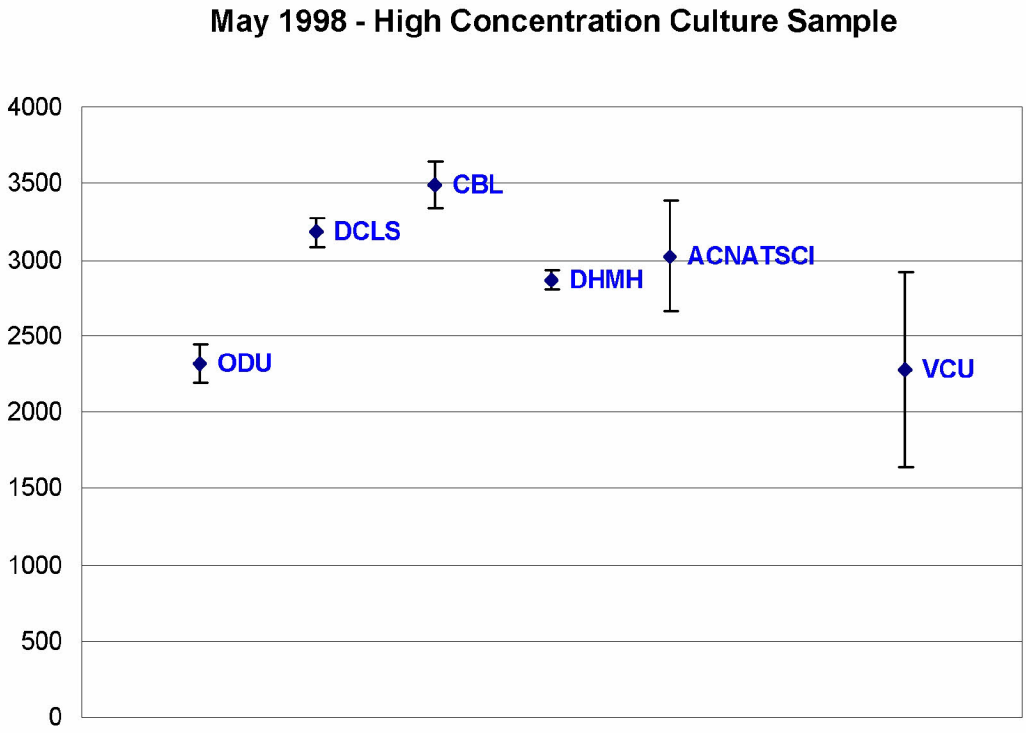
The graphs below depict the results of these splits.






December 1997 - Station LE2.3
15.0
12.0
9.0
6.0
3.0
0.0
CBL
VCU
DCLS
ACNATSCI
CRL
ODU
DHMH


May 1998 - Low Concentration Natural Sample
14
12
10
8
6
4
2
0
CBL
ACNATSCI
DCLS
DHMH
ODU
VCU


May 1998 - High Concentration Culture Sample
4000
3500
3000
2500
2000
1500
1000
500
0
CBL
DCLS
DHMH
ACNATSCI
ODU
VCU

Appendix A

Table A - Percent recovery data from spiked sample for Old Dominion University. Values are percentages of concentrations measured reletive to concentrations expected. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

		PP	TDN	Si	NH4	TDP	PO4f	NO23	NO2	DOC
1994-1998	Mean	*100.5*	*101.0*	*98.4*	*101.9*	*98.5*	*95.3*	*99.2*	*99.8*	*100.3*
	Median	*100.9*	*100.0*	*99.0*	*104.0*	*99.0*	*95.5*	*99.0*	*99.0*	*101.0*
	Min	*91.5*	*89.0*	*81.0*	*91.0*	*90.0*	*86.0*	*94.0*	*95.0*	*93.0*
	Max	*109.9*	*118.0*	*109.0*	*109.0*	*105.0*	*103.0*	*107.0*	*108.0*	*104.0*
	Stand. Dev.	*4.6*	*6.3*	*7.9*	*5.9*	*3.7*	*4.3*	*3.0*	*3.6*	*3.2*
1997-1998	Mean	*102.4*	*100.0*	*95.0*	*105.8*	*97.5*	*94.0*	*97.0*	*99.3*	
	Median	*102.5*	*100.0*	*95.5*	*108.0*	*96.5*	*94.0*	*97.0*	*99.5*	
	Min	*97.8*	*98.0*	*88.0*	*99.0*	*93.0*	*90.0*	*94.0*	*98.0*	
	Max	*106.5*	*101.0*	*103.0*	*109.0*	*105.0*	*98.0*	*99.0*	*100.0*	
	Stand. Dev.	*2.8*	*1.1*	*5.4*	*4.1*	*4.0*	*2.8*	*2.1*	*0.8*	
	3/7/94	95	108	109		99		98	95	104
	5/2/94	92	95		99			99	108	99.5
	8/15/94	96	89	100		97	100			101
	11/14/94	101	111	102	99	97	98	107	101	101
	2/13/95	110	118	106	96	103	98	103	102	101
	5/8/95	99		109	93	100	98	100	104	102
	8/7/95	102	101	106	104	100	98	97	99	101
	11/13/95	101	102	103	97	102	98	99	107	93
	4/8/96	94	105		109	100	95	100	98	
	5/13/96	100	97.2	106	109	103	95	101	98	
	8/5/96	104	99	81	104	100	103	96	98	
	11/20/96		99	90	97	95	88	103	95	
	3/4/97	105	101	94	105	101	95	99	100	
	6/9/97	96	94	95	91	90	86	99	95	
	9/8/97	103	100	88	108	97	94	97	99	
	12/8/97	102	98	90		98	90		100	
	3/23/98	103	100	98	99	96	92	99	100	
	6/11/98	107	101	95	105	105	96	99	98	
	9/1/98	102	100	103	108	96	98	94	100	
	12/15/98	98	101	96	109	93	94	96	99	

Table B - Percent recovery data from spiked sample for Chesapeake Biological Laboratory. Values are percentages of concentrations measured reletive to concentrations expected. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

		PP	TDN	Si	NH4	TDP	PO4f	NO23	NO2	DOC
1994-1998	Mean	*99.9*	*99.7*	*93.9*	*96.4*	*97.9*	*98.4*	*104.4*	*99.1*	*102.2*
	Median	*100*	*99*	*93.5*	*96.5*	*97*	*97.5*	*104*	*99*	*102*
	Min	*96*	*95*	*91*	*88*	*93*	*92*	*99*	*96*	*100*
	Max	*103*	*108*	*97*	*106*	*103*	*104*	*115*	*105*	*104*
	Stand. Dev.	*2.0*	*3.3*	*1.7*	*4.1*	*2.9*	*3.9*	*4.4*	*2.3*	*1.7*
1997-1998	Mean	101.1	101.1	93.5	96.5	98.3	97.3	103	99.8	
	Median	101	100.5	94	96.5	98.5	96.5	101.5	100	
	Min	100	95	91	93	93	92	100	98	
	Max	103	108	96	99	103	103	110	102	
	Stand. Dev.	1.2	4.4	1.8	2.1	4.2	4.1	3.9	1.7	
	3/7/94		103	93	88	99	97	103	98	103
	5/2/94	100	96	97	100	98	96	99	105	
	8/15/94	102	97	93	97	97	94	115	96	100
	11/14/94	99	100	93	92	101	101	107	97	101
	2/13/95	96	96	93	92	95	104	110	99	104
	5/8/95		96	93	101	94	101	110	98	101
	8/7/95			93	99		103	104	100	104
	11/13/95	99	103	91	96	98	92	101	99	
	4/8/96	96	99	93	106	99	96	106	97	
	5/13/96	100	98	96	96	96	97	100	96	
	8/5/96	98	100	95	90	102	100	107	100	
	11/20/96	101	102	95	97	97	97	99	96	
	3/4/97	102	98	95	99	97	104	104	101	
	6/9/97	99	99	96	96	97	102	104	101	
	9/8/97	102	100	96	96	96	101	110	101	
	12/8/97	101	104	91	93	101	103	101	102	
	3/23/98	100	99	94	99	103	95	102	101	
	6/11/98	101	95	94	98	93	95	105	99	
	9/1/98	100	101	94	97	95	98	100	98	
	12/15/98	103	108	92	96	102	92	100	98	

Table C - Percent recovery data from spiked sample for Division of Consolidated Laboratory Services. Values are percentages of concentrations measured reletive to concentrations expected. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

		PP	TDN	SiO2	NH4	TDP	PO4f	TP	NO2	TKNw
1994-1998	Mean	*102.3*	*91.0*	*99.5*	*106.1*	*93.9*	*93.9*	*99.9*	*100.1*	*97.8*
	Median	*99.0*	*93.0*	*100.0*	*105.0*	*93.0*	*94.0*	*99.0*	*100.0*	*100.0*
	Min	*96.0*	*62.0*	*93.0*	*85.0*	*78.0*	*85.0*	*82.0*	*70.0*	*94.0*
	Max	*113.0*	*103.0*	*102.0*	*153.0*	*104.0*	*102.0*	*129.0*	*114.0*	*100.0*
	Stand. Dev.	*6.1*	*10.6*	*2.5*	*16.1*	*6.5*	*4.5*	*11.0*	*8.7*	*3.0*
1997-1998	Mean	*103.8*	*95.5*	*98.3*	*100.0*	*95.3*	*92.0*	*104.0*	*94.3*	
	Median	*104.5*	*95.0*	*99.5*	*100.0*	*94.5*	*91.0*	*99.0*	*101.0*	
	Min	*96.0*	*89.0*	*93.0*	*90.0*	*93.0*	*91.0*	*95.0*	*70.0*	
	Max	*110.0*	*103.0*	*101.0*	*110.0*	*99.0*	*95.0*	*118.0*	*105.0*	
	Stand. Dev.	*5.9*	*6.0*	*3.6*	*10.0*	*2.9*	*2.0*	*12.3*	*16.3*	
3/7/94				102	110	100	96	100	100	100
5/2/94				100		100	100	100	98	100
8/15/94				102	108	91	90	91	100	94
11/14/94				100	98	92	88	92	100	100
2/13/95				94	104	78	93	100	95	95
5/8/95		97	95	100	109	98	95	82	102	
8/7/95		96	99	102	108	97	95	92	103	
11/13/95		99	94	98	99	84	97	92	98	
4/8/96		108	88	100	153	91	93	100	105	
5/13/96		97				88	102	108	99	
8/5/96		113		100		93	90	108	100	
11/20/96		98	91	100	105	100	98	98	100	
3/4/97		109	62	100		104	100	95	110	
6/9/97		98	90	100	85		85	129	114	
9/8/97		110	97	93	100	96	91		70	
12/8/97		103	93	100	90	93	95	118	100	
3/23/98										
6/11/98										
9/1/98		96	89	99		99	91	99	102	
12/15/98		106	103	101	110	93	91	95	105	

Table D - Percent recovery data from spiked sample for Maryland Department of Health and Mental Hygene. Values are percentages of concentrations measured reletive to concentrations expected. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

		DOC	NO23	Si	NH4	TDP	PO4f	TP	NO2	TKNw
1994-1998	Mean	*101.4*	*102.7*	*95.7*	*98.4*	*98.9*	*94.9*	*98.7*	*102.0*	*105.2*
	Median	*104.0*	*102.5*	*95.0*	*98.0*	*99.5*	*98.0*	*100.0*	*102.0*	*106.5*
	Min	*68.0*	*95.0*	*90.0*	*91.0*	*81.0*	*78.0*	*76.0*	*98.0*	*90.0*
	Max	*129.0*	*108.0*	*101.0*	*106.0*	*105.0*	*102.0*	*113.0*	*108.0*	*116.0*
	Stand. Dev.	*14.0*	*3.5*	*3.6*	*5.0*	*5.3*	*6.3*	*8.9*	*2.4*	*8.0*
1997-1998	Mean	*98.5*	*104.5*	*96.8*	*100.3*	*98.2*	*98.3*	*97.0*	*100.7*	*95.8*
	Median	*98.0*	*105.5*	*97.5*	*101.0*	*98.0*	*100.0*	*96.0*	*101.0*	*97.0*
	Min	*93.0*	*99.0*	*91.0*	*93.0*	*94.0*	*92.0*	*92.0*	*98.0*	*90.0*
	Max	*106.0*	*108.0*	*100.0*	*106.0*	*101.0*	*100.0*	*105.0*	*102.0*	*101.0*
	Stand. Dev.	*5.2*	*3.4*	*3.4*	*5.9*	*2.9*	*3.2*	*5.0*	*1.6*	*4.1*
	3/7/94	71	100	90	97	81	98	76	104	109
	5/2/94	113	104	95	97	105	102	110	104	103
	8/15/94	129	107	99	100		99		104	
	11/14/94	68	95	95	106	100	92	104	101	112
	2/13/95	112	102	93	100	104	100	108	99	108
	5/8/95	107	99		92	103	90	102	100	99
	8/7/95	110	103	90	99	103	96	101	100	99
	11/13/95	105	101	95		98	86	100	102	109
	4/8/96	104	100			98		100	106	115
	5/13/96	104	108	99	94	98	90	113	100	115
	8/5/96	98	99	91	91	101	78	98	102	105
	11/20/96	117	101	98	106	98	90	85	102	110
	3/4/97	106	104	95	94	99	92	92	108	116
	6/9/97	93	104	101	98	102	100	103	104	114
	9/8/97	101	107	98		101	92	105	102	97
	12/8/97	102	106	100		94	100	92	102	97
	3/23/98	106	99	91	98		100		100	
	6/11/98	93	105	97	106	98	98	94	100	94
	9/1/98	95	108	95	93	97	100	98	102	101
	12/15/98	94	102	100	104	101	100	96	98	90

Table E - SRM data for Old Dominion University. The SRM_EPA values are the known concentrations of the SRMs, SRM_DE values are the concentrations that were measured and the % Recov values are the percentages of the SRM_Des relative to the SRM_EPAs. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

	PP Samp	PP SRM_EPA	PP SRM_DE	PP % Recov	TDN Samp	TDN SRM_EPA	TDN SRM_DE	TDN % Recov	PO4f Samp	PO4f SRM_EPA	PO4f SRM_DE	PO4f % Recov
3/7/94	0.00	0.50	0.52	103.40	0.00	0.25	0.235	94.00	0.00	0.02	0.02	100.00
5/2/94	0.00	0.50	0.48	96.40	0.00	0.4	0.412	103.00	0.00	0.02	0.0185	92.50
8/15/94	0.00	0.50	0.48	95.60	0.00	0.4	0.408	102.00				
11/14/94	0.00	0.50	0.51	101.20	0.00	0.4	0.374	93.50	0.00	0.02	0.022	110.00
2/13/95	0.00	0.50	0.48	95.20	0.00	0.4	0.4	100.00	0.005	0.02	0.027	108.00
5/8/95	0.00	0.50	0.47	93.60	0.00	0.4	0.401	100.25	0.001	0.02	0.022	104.76
8/7/95	0.00	0.50	0.48	95.00	0.00	0.4	0.381	95.25	0.00	0.02	0.021	105.00
11/13/95	0.00	0.50	0.50	100.20	0.00	0.4	0.404	101.00	0.001	0.02	0.019	90.48
4/8/96	0.00	0.50	0.49	97.00	0.00	0.4	0.417	104.25	0.00	0.02	0.018	90.00
5/13/96	0.00	0.50	0.46	92.60	0.00	0.4	0.395	98.75	0.00	0.02	0.02	100.00
8/5/96	0.00	0.50	0.49	98.20	0.00	0.4	0.397	99.25	0.00	0.02	0.021	105.00
11/20/96					0.00	0.4	0.397	99.25	0.00	0.02	0.015	75.00
3/4/97	0.00	0.50	0.51	101.60	0.00	0.4	0.399	99.75	0.00	0.04	0.039	97.50
6/9/97					0.00	0.4	0.4	100.00	0.00	0.04	0.04	100.00
9/8/97	0.00	0.75	0.77	103.29	0.00	0.4	0.407	101.75	0.00	0.04	0.0391	97.75
12/8/97					0.00	0.4	0.398	99.50	0.00	0.0375	0.0378	100.80
3/23/98	0.00	0.75	0.77	103.05	0.00	0.4	0.403	100.75	0.00	0.0375	0.0382	101.87
6/11/98	0.00	0.75	0.78	103.85	0.00	0.21	0.1967	93.67	0.00	0.0375	0.038	101.33
9/1/98	0.00	0.75	0.72	96.05	0.00	0.21	0.198	94.29	0.00	0.0375	0.0376	100.27
12/15/98	0.00	1.00	0.99	99.30	0.00	0.21	0.197	93.81	0.00	0.04	0.0387	96.75

	NH4 Samp	NH4 SRM_EPA	NH4 SRM_DE	NH4 % Recov	TDP Samp	TDP SRM_EPA	TDP SRM_DE	TDP % Recov	NO23 Samp	NO23 SRM_EPA	NO23 SRM_DE	NO23 % Recov
3/7/94	0.00	0.04	0.04	110.00	0.00	0.15	0.154	102.67	0.00	0.04	0.04	96.50
5/2/94	0.00	0.04	0.04	94.00	0.00	0.15	0.148	98.67	0.00	0.04	0.04	99.75
8/15/94	0.00	0.04	0.04	107.75	0.01	0.15	0.159	99.38	0.00	0.04	0.04	97.75
11/14/94	0.00	0.04	0.04	96.50	0.006	0.15	0.158	101.28	0.00	0.04	0.04	94.00
2/13/95	0.00	0.04	0.04	96.75	0.013	0.15	0.16	98.16	0.00	0.04	0.04	99.25
5/8/95	0.00	0.04	0.04	94.25	0.003	0.15	0.149	97.39	0.00	0.04	0.04	100.00
8/7/95	0.00	0.04	0.04	102.25	0.00	0.15	0.145	96.67	0.00	0.04	0.04	100.75
11/13/95	0.00	0.04	0.04	96.50	0.00	0.15	0.155	103.33	0.00	0.04	0.04	101.75
4/8/96	0.00	0.04	0.04	102.75	0.00	0.15	0.154	102.67	0.00	0.04	0.04	96.00
5/13/96	0.00	0.04	0.04	102.75	0.00	0.15	0.156	104.00	0.00	0.04	0.04	98.50
8/5/96	0.00	0.04	0.04	98.00	0.00	0.15	0.149	99.33	0.00	0.04	0.04	99.00
11/20/96	0.00	0.04	0.04	97.00	0.00	0.15	0.135	90.00	0.00	0.04	0.04	98.75
3/4/97	0.00	0.04	0.04	99.50	0.00	0.12	0.123	102.50	0.00	0.20	0.20	98.80
6/9/97	0.00	0.04	0.04	94.50	0.00	0.12	0.1218	101.50	0.00	0.20	0.20	99.50
9/8/97	0.00	0.03	0.03	98.39	0.00	0.12	0.1203	100.25	0.00	0.04	0.04	100.86
12/8/97	0.00	0.03	0.03	100.97	0.00	0.12	0.1216	101.33	0.00	0.04	0.04	101.14
3/23/98	0.00	0.03	0.03	100.00	0.00	0.06	0.0591	98.50	0.00	0.035	0.0358	102.29
6/11/98	0.00	0.03	0.03	95.16	0.00	0.105	0.1005	95.71	0.00	0.035	0.0345	98.57
9/1/98	0.00	0.03	0.03	105.48	0.00	0.105	0.1007	95.90	0.00	0.035	0.0348	99.43

12/15/98	0.00	0.08	0.08	97.50	0.00	0.105	0.0979	93.24	0.00	0.08	0.0778	97.25

	DOC Samp	DOC SRM_EPA	DOC SRM_DE	DOC % Recov
3/7/94	0.22	6.15	6.39	100.31
5/2/94	0.49	6.15	6.6	99.40
8/15/94	0.49	6.15	6.6	99.40
11/14/94	0.15	6.15	6.52	103.49
2/13/95	0.015	6.15	6.52	105.76
5/8/95	0.028	6.15	6.18	100.03
8/7/95	0.03	6.15	6.27	101.46
11/13/95	0.17	6.15	6.4	101.27

Table F - SRM data for Chesapeake Biological Laboratory. The SRM_EPA values are the known concetrations of the SRMs, SRM_DE values are the concentrations that were measured and the % Recov values are the percentages of the SRM_Des relative to the SRM_EPAs. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

	NH4 Samp	NH4 SRM_EPA	NH4 SRM_DE	NH4 % Recov	TDN Samp	TDN SRM_EPA	TDN SRM_DE	TDN % Recov	PO4f Samp	PO4f SRM_EPA	PO4f SRM_DE	PO4f % Recov
3/7/94	0	0.2	0.192	96.00	0	0.5	0.502	100.40	0	0.039	0.0406	104.10
5/2/94	0	0.2	0.208	104.00	0	0.5	0.52	104.00	0	0.039	0.0359	92.05
8/15/94	0	0.2	0.195	97.50	0	0.5	0.54	108.00	0	0.039	0.0384	98.46
11/14/94	0	0.2	0.198	99.00	0	0.5	0.54	108.00	0	0.039	0.0367	94.10
2/13/95	0	0.2	0.188	94.00	0	0.5	0.55	110.00	0			
5/8/95	0	0.2	0.203	101.50	0	0.5	0.55	110.00	0	0.039	0.0365	93.59
8/7/95	0	0.2	0.199	99.50	0	0.5	0.55	110.00	0	0.05	0.0501	100.20
11/13/95	0	0.2	0.199	99.50	0	0.5	0.51	102.00	0	0.05	0.0497	99.40
4/8/96	0	0.2	0.203	101.50	0	0.5	0.53	106.00	0	0.05	0.0474	94.80
5/13/96	0	0.2	0.196	98.00	0	0.5	0.5	100.00	0	0.05	0.0498	99.60
8/5/96	0	0.2	0.203	101.50	0	0.5	0.55	110.00	0	0.05	0.0511	102.20
11/20/96	0	0.2	0.192	96.00	0	0.5	0.5	100.00	0	0.05	0.0493	98.60
3/4/97	0	0.2	0.205	102.50	0	0.5	0.55	110.00	0	0.05	0.0508	101.60
6/9/97	0	0.2	0.204	102.00	0	0.5	0.51	102.00	0	0.05	0.05	100.00
9/8/97	0	0.2	0.198	99.00	0	0.5	0.52	104.00	0	0.05	0.051	102.00
12/8/97	0				0	0.5	0.56	112.00	0	0.05	0.0475	95.00
3/23/98	0	0.155	0.172	110.97	0	0.42	0.43	102.38				
6/11/98	0	0.155	0.16	103.23	0				0	0.075	0.0811	108.13
9/1/98	0	0.155	0.157	101.29	0	0.42	0.43	102.38	0	0.075	0.0815	108.67
12/15/98	0	0.2	0.194	97.00	0	0.375	0.41	109.33	0	0.05	0.0527	105.40

	NO23 Samp	NO23 SRM_EPA	NO23 SRM_DE	NO23 % Recov	TDP Samp	TDP SRM_EPA	TDP SRM_DE	TDP % Recov
3/7/94	0	0.2	0.198	99.00	0	0.15	0.153	102.00
5/2/94	0	0.2	0.199	99.50	0	0.15	0.152	101.33
8/15/94	0	0.2	0.201	100.50	0	0.15	0.148	98.67
11/14/94	0	0.2	0.2	100.00	0	0.15	0.145	96.67
2/13/95	0	0.2	0.199	99.50	0	0.15	0.1509	100.60
5/8/95	0	0.2	0.21	105.00	0	0.15	0.1596	106.40
8/7/95	0	0.2	0.191	95.50	0	0.15	0.1482	98.80
11/13/95	0	0.2	0.201	100.50	0	0.15	0.1517	101.13
4/8/96	0	0.2	0.195	97.50	0	0.15	0.139	92.67
5/13/96	0	0.2	0.197	98.50	0	0.15	0.141	94.00
8/5/96	0				0	0.15	0.164	109.33
11/20/96	0	0.2	0.206	103.00	0	0.15	0.148	98.67
3/4/97	0	0.2	0.205	102.50	0	0.15	0.142	94.67
6/9/97	0	0.2	0.204	102.00	0	0.15	0.141	94.00
9/8/97	0	0.2	0.191	95.50	0	0.15	0.164	109.33
12/8/97	0	0.2	0.196	98.00	0	0.15	0.155	103.33
3/23/98					0	0.205	0.198	96.59
6/11/98	0	0.175	0.192	109.71				
9/1/98	0	0.175	0.205	117.14	0	0.205	0.198	96.59
12/15/98	0	0.2	0.225	112.50	0	0.15	0.1498	99.87

Table G - SRM data for the Division of Consolidated Laboratory Services. The SRM_EPA values are the known concentrations of the SRMs, SRM_DE values are the concentrations that were measured and the % Recov values are the percentages of the SRM_Des relative to the SRM_EPAs. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem.

	NH4 Samp	NH4 SRM_EPA	NH4 SRM_DE	NH4 % Recov	TDN Samp	TDN SRM_EPA	TDN SRM_DE	TDN % Recov	Si Samp	Si SRM_EPA	Si SRM_DE	Si % Recov
3/7/94	0.00	0.07	0.08	114.29								
5/2/94	0.00	0.07	0.078	111.43								
8/15/94												
11/14/94	0.00	0.30	0.317	105.67								
2/13/95	0.00	0.30	0.324	108.00								
5/8/95												
8/7/95	0.00	0.30	0.319	106.33								
11/13/95												
4/8/96									0.00	0.50	0.55	110.00
5/13/96	0.00	0.06	0.066	110.00					0.00	0.50	0.51	102.00
8/5/96	0.00	0.30	0.276	92.00					0.00	0.50	0.42	84.00
11/20/96												
3/4/97					0.00	0.48	0.497	103.54	0.00	0.50	0.53	106.00
6/9/97									0.00	0.50	0.55	110.00
9/8/97	0.00	0.30	0.325	108.33	0.00	0.48	0.491	102.29	0.00	0.50	0.49	98.00
12/8/97	0.00	0.30	0.331	110.33	0.00	0.48	0.493	102.71	0.00	0.50	0.56	112.00
3/23/98												
6/11/98												
9/1/98	0.00	0.046	0.049	106.52	0.00	0.48	0.456	95.00	0.00	0.50	0.54	108.00
12/15/98	0.00	0.046	0.051	110.87	0.00	0.48	0.478	99.58	0.00	0.54	0.50	92.59

	TP Samp	TP SRM_EPA	TP SRM_DE	TP % Recov	TDP Samp	TDP SRM_EPA	TDP SRM_DE	TDP % Recov	PO4f Samp	PO4f SRM_EPA	PO4f SRM_DE	PO4f % Recov
3/7/94	0.00	0.75	0.72	96.00	0.00	0.75	0.72	96.00	0.00	0.10	0.077	77.00
5/2/94												
8/15/94	0.00	0.75	0.68	90.67	0.00	0.75	0.68	90.67	0.00	0.195	0.192	98.46
11/14/94	0.00	0.75	0.75	100.00	0.00	0.75	0.75	100.00	0.00	0.075	0.073	97.33
2/13/95	0.00	1.50	1.60	106.67					0.00	0.075	0.077	102.67
5/8/95												
8/7/95									0.00	0.075	0.068	90.67
11/13/95									0.00	0.075	0.074	98.67
4/8/96	0.00	4.76	4.66	97.90								
5/13/96	0.00	4.76	4.55	95.59					0.00	0.015	0.016	106.67
8/5/96	0.00	4.76	4.31	90.55					0.00	0.075	0.073	97.33
11/20/96	0.00	4.76	4.77	100.21								
3/4/97	0.00	2.10	2.24	106.67	0.00	0.046	0.051	110.87				
6/9/97	0.00	0.31	0.30	96.77	0.00	0.046	0.049	106.52				
9/8/97					0.00	0.046	0.049	106.52	0.00	0.075	0.073	97.33
12/8/97	0.00	0.23	0.23	100.00	0.00	0.046	0.046	100.00	0.00	0.075	0.075	100.00
3/23/98												
6/11/98												
9/1/98	0.00	0.046	0.046	100.00	0.00	0.046	0.046	100.00	0.00	0.06	0.062	103.33
12/15/98	0.00	0.046	0.047	102.17	0.00	0.046	0.049	106.52	0.00	0.06	0.062	103.33

	TKNw Samp	TKNw SRM_EPA	TKNw SRM_DE	TKNw % Recov
3/7/94	0.00	2.50	2.40	96.00
5/2/94	0.00	2.50	2.40	96.00
8/15/94	0.00	2.50	2.00	80.00
11/14/94				
2/13/95	0.00	6.50	6.40	98.46

Table H - SRM data for the Maryland Department of Health and Mental Hygene. The SRM_EPA values are the known concentrations of the SRMs, SRM_DE values are the concentrations that were measured and the % Recov values are the percentages of the SRM_Des relative to the SRM_EPAs. Percentages should be >90% or <110%. Percentages <80% or >120% are indicative of a problem. SRM data for 1998 were not available at the time of this report.

	TOC Samp	TOC SRM_EPA	TOC SRM_DE	TOC % Recov	TP Samp	TP SRM_EPA	TP SRM_DE	TP % Recov	Si Samp	Si SRM_EPA	Si SRM_DE	Si % Recov
2/8/94	0											
3/7/94	0											
5/2/94	0											
11/14/94	0				0	1.5	1.56	104.00				
2/13/95	0				0							
5/8/95	0				0	1.5	1.61	107.33				
8/7/95	0				0	1.5		0.00				
11/13/95	0	40.9	40.9	100.00	0	1.5	1.53	102.00				
4/8/96	0	40.9	42.8	104.65	0	1.5	1.45	96.67				
5/13/96	0	40.9	41.3	100.98	0	1.5	1.35	90.00				
8/5/96	0	40.9	42.8	104.65	0	1.5	1.58	105.33				
11/20/96	0	40.9	40.2	98.29	0	1.5	1.35	90.00				
3/4/97	0	40.9	38.1	93.15	0	5	4.86	97.20				
6/9/97	0	40.9	37.6	91.93	0	5	4.54	90.80	0	1	1.05	105.00
9/8/97	0	40.9	40.7	99.51	0	1.5	1.46	97.33	0	4	3.99	99.75
12/8/97	0	40.9	43.0	105.13	0	1.5	1.47	98.00	0	1	1.05	105.00

	NH4 Samp	NH4 SRM_EPA	NH4 SRM_DE	NH4 % Recov	NO2 Samp	NO2 SRM_EPA	NO2 SRM_DE	NO2 % Recov	PO4f Samp	PO4f SRM_EPA	PO4f SRM_DE	PO4f % Recov
2/8/94	0	2.0	2.04	102.00					0	0.39	0.4	102.56
3/7/94	0	2.0	1.97	98.50					0	0.39	0.425	108.97
5/2/94	0	2.0	1.88	94.00					0	0.39		0.00
11/14/94	0	2.0	1.925	96.25					0	0.39	0.385	98.72
2/13/95	0	2.0	2.035	101.75	0	0.113	0.113	100.00	0	0.39	0.4	102.56
5/8/95	0	2.0	1.9	95.00	0	0.102	0.097	95.10	0	0.39	0.385	98.72
8/7/95	0				0							
11/13/95	0	2.0	1.935	96.75	0	0.102	0.101	99.02	0	0.39	0.405	103.85
4/8/96	0	2.0	1.955	97.75	0	0.102	0.1	98.04	0	0.39	0.39	100.00
5/13/96	0	2.0	1.955	97.75	0	0.102	0.103	100.98	0	0.39	0.38	97.44
8/5/96	0	2.0	1.965	98.25	0	0.102	0.104	101.96	0	0.39	0.36	92.31
11/20/96	0	2.0	2.07	103.50	0	0.102	0.105	102.94	0	0.39	0.345	88.46
3/4/97	0				0	0.102	0.106	103.92	0	0.5	0.465	93.00
6/9/97	0	2.0	1.985	99.25	0	0.102	0.101	99.02	0	0.5	0.465	93.00
9/8/97	0	2.0	1.99	99.50	0	0.102	0.111	108.82	0	0.5	0.47	94.00
12/8/97	0	2.0	2.14	107.00	0	0.113	0.114	100.88	0	0.5	0.46	92.00

	NO23 Samp	NO23 SRM_EPA	NO23 SRM_DE	NO23 % Recov	TKNw Samp	TKNw SRM_EPA	TKNw SRM_DE	TKNw % Recov
2/8/94	0	0.93	1.005	108.06	0			
3/7/94	0	2.0	2.115	105.75	0			
5/2/94	0	2.0	2.153	107.65	0			
11/14/94	0	2.0	2.14	107.00	0	5.0	4.865	97.30
2/13/95	0	2.0	2.02	101.00	0	5.0	4.635	92.70
5/8/95	0	2.0	1.94	97.00	0	1.5	1.54	102.67
8/7/95	0				0			
11/13/95	0	2.0	2.01	100.50	0	5.0	5.001	100.02
4/8/96	0	2.0	2.02	101.00	0	5.0	5.001	100.02
5/13/96	0	2.0	1.96	98.00	0	5.0	4.323	86.46
8/5/96	0	2.0	1.93	96.50	0	5.0	5.102	102.04
11/20/96	0	2.0	2.06	103.00	0	5.0	4.351	87.02
3/4/97	0	2.0	2.02	101.00	0	5.0	4.546	90.92
6/9/97	0	2.0	2.06	103.00	0	5.0	4.767	95.34
9/8/97	0	2.0	2.15	107.50	0	5.0	5.05	101.00
12/8/97	0	2.0	2.02	101.00	0	5.0	4.9	98.00

Table I - Coefficients of Variation (CVs) by parameter, lab and date. CVs are the standard deviation of the three replicates analyzed by a lab on a particular date expressed as a percentage of the mean of those three replicates.CVs should be consitently less than 25% across dates.

	TDP				PP				PO4F			
	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS
3/7/94	14.5	13.6	ND	0.0	5.8	0.0	ND	0.0	45.3	0.0	52.7	ND
5/2/94	7.1	ND	34.6	ND	3.7	2.8	86.7	21.7	1.9	ND	16.7	0.0
8/15/94	9.4	2.3	17.0	21.7	5.3	2.2	10.8	17.3	18.2	14.3	0.0	13.3
11/14/94	8.7	10.0	8.7	34.6	3.5	7.1	141.4	43.3	22.9	11.9	0.0	0.0
2/13/95	13.4	6.0	ND	43.3	0.8	5.3	32.8	15.7	29.6	9.1	ND	0.0
5/8/95	5.4	22.9	15.1	10.8	9.8	0.0	59.3	29.3	15.5	24.7	0.0	0.0
8/7/95	4.2	7.9	27.2	2.6	4.8	3.3	86.9	4.0	6.2	4.3	20.0	0.0
11/13/95	4.6	0.0	9.1	3.2	0.6	11.5	16.4	2.4	71.3	12.5	9.9	0.0
4/8/96	5.4	0.0	20.4	74.8	2.1	0.0	40.1	2.0	87.6	ND	0.0	0.0
5/13/96	0.7	12.4	58.3	16.7	7.8	3.5	55.5	0.8	85.4	34.6	11.9	13.3
8/5/96	2.2	4.0	7.4	3.3	4.2	5.9	46.7	4.3	3.0	6.9	ND	6.7
11/20/96	8.6	62.4	29.7	27.0	0.8	ND	53.7	0.8	41.4	ND	52.9	10.8
3/4/97	10.7	13.3	34.6	22.3	4.5	4.5	66.1	6.7	7.4	ND	45.4	ND
6/9/97	1.4	0.0	23.3	18.4	3.9	2.9	45.1	6.9	4.2	ND	7.4	33.3
9/8/97	4.6	5.5	41.6	2.7	0.8	5.3	20.0	4.7	42.8	4.6	0.0	10.8
12/8/97	3.5	7.0	18.7	0.0	5.7	0.0	33.1	0.0	0.0	ND	ND	15.7
3/23/98	7.7	19.9	25.0	8.7	5.1	0.0	8.3	0.0	50.8	14.7	0.0	0.0
6/11/98	6.6	1.4	29.4	ND	2.4	2.4	8.9	ND	9.4	1.0	6.7	ND
9/1/98	2.5	3.5	1.4	1.9	3.9	2.0	5.8	2.7	22.1	1.6	5.6	0.0
12/14/98	17.1	9.2	11.3	0.0	7.7	5.2	24.7	2.1	46.8	41.7	15.7	0.0

	TP				TDN				NH4			
	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS
3/7/94	8.6	5.2	ND	0.0	5.5	1.8	5.5	ND	25.0	17.0	ND	4.8
5/2/94	2.1	24.0	47.0	0.0	4.0	2.6	24.7	ND	1.4	9.8	74.5	4.6
8/15/94	3.6	1.9	9.3	0.0	22.8	1.8	ND	ND	104.4	ND	ND	35.0
11/14/94	4.2	4.2	14.6	0.0	4.2	2.9	2.9	ND	22.2	4.3	8.6	8.7
2/13/95	3.8	2.0	32.8	0.0	3.2	3.4	3.3	ND	95.2	82.2	24.7	11.4
5/8/95	7.3	9.2	18.0	0.0	3.9	0.0	4.0	6.3	51.6	40.1	46.9	8.7
8/7/95	1.3	2.9	4.0	9.1	9.8	4.6	4.5	3.8	8.5	9.0	5.8	1.0
11/13/95	3.1	4.9	3.7	0.0	6.2	3.0	ND	0.3	11.3	2.8	5.5	9.8
4/8/96	3.3	0.0	10.2	0.0	1.7	1.7	1.2	17.6	12.9	14.8	0.0	4.2
5/13/96	5.4	2.7	44.2	17.3	3.1	0.5	3.3	2.0	6.3	1.1	0.0	9.0
8/5/96	1.1	3.7	11.8	0.0	4.7	8.3	ND	3.7	20.1	15.6	5.9	24.7
11/20/96	2.1	ND	13.6	10.8	0.7	2.3	7.1	3.4	32.7	50.9	7.5	16.7
3/4/97	3.5	5.3	14.1	0.0	3.4	0.7	1.3	2.6	1.3	1.5	9.2	7.0
6/9/97	1.8	2.0	4.6	12.4	6.2	1.1	4.9	0.1	5.1	9.9	17.6	49.9
9/8/97	2.2	1.0	15.5	ND	4.9	3.5	ND	2.1	55.3	58.5	2.8	9.4
12/8/97	4.2	3.3	7.8	10.8	4.2	0.8	22.5	3.5	13.9	15.7	7.5	23.6
3/23/98	3.0	3.2	11.0	13.3	2.8	0.2	1.4	1.5	4.7	2.9	1.4	5.5
6/11/98	3.3	2.0	11.2	ND	3.1	1.4	1.1	ND	50.7	14.8	86.6	ND
9/1/98	0.8	1.3	1.7	0.0	6.4	2.7	5.8	6.3	48.5	3.9	0.0	ND
12/14/98	7.7	5.0	3.9	15.6	17.7	0.2	1.7	2.0	0.0	7.8	3.3	13.9

	NO23				NO2				TSS			
	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS
3/7/94	0.5	2.8	2.6	0.3	3.5	5.8	7.1	0.0	20.4	12.0	10.2	ND
5/2/94	1.4	0.7	19.9	0.6	2.3	0.2	31.0	0.0	14.3	1.7	11.5	ND
8/15/94	61.7	ND	ND	ND	17.3	0.0	0.0	ND	8.7	11.4	69.6	ND
11/14/94	8.1	0.5	9.3	0.0	20.7	1.8	0.0	0.0	8.8	3.9	22.3	ND
2/13/95	2.1	1.8	0.4	0.5	2.4	0.0	10.2	0.0	7.8	5.1	2.8	ND
5/8/95	0.6	0.4	1.0	0.5	16.0	2.2	0.0	0.0	13.6	ND	34.3	ND
8/7/95	6.6	8.9	11.1	ND	7.5	2.5	0.0	0.0	8.9	32.4	24.1	ND
11/13/95	4.4	1.0	2.7	24.7	2.5	6.9	0.0	0.0	18.6	1.2	24.1	19.9
4/8/96	2.0	17.1	0.7	0.6	32.6	8.3	8.3	4.3	9.4	11.0	43.3	ND
5/13/96	0.8	6.1	0.4	0.5	2.2	5.8	2.3	1.9	6.0	1.1	10.6	0.0
8/5/96	64.3	17.3	ND	ND	68.5	10.8	0.0	ND	8.2	6.5	22.9	ND
11/20/96	1.0	9.1	0.6	0.6	0.8	0.7	2.4	0.0	12.8	ND	18.3	0.0
3/4/97	12.3	0.6	3.5	1.1	0.8	2.5	0.0	0.0	3.4	19.6	20.8	ND
6/9/97	0.2	2.5	1.2	0.8	2.1	3.7	0.0	0.0	13.5	4.0	11.9	60.3
9/8/97	64.0	16.7	ND	ND	68.7	50.0	21.7	ND	6.1	5.1	43.3	ND
12/8/97	1.0	13.2	1.2	1.0	30.3	6.4	0.0	21.7	8.6	10.1	6.2	0.0
3/23/98	0.3	0.4	1.2	2.2	5.1	0.5	0.0	0.0	13.0	12.4	19.9	0.0
6/11/98	0.6	0.6	0.2	ND	20.8	1.3	10.8	ND	7.5	4.7	15.7	ND
9/1/98	57.5	56.8	34.6	0.0	23.1	0.0	0.0	0.0	7.0	13.2	32.8	36.5
12/14/98	17.1	15.6	0.0	0.0	4.7	11.1	0.0	0.0	14.5	20.7	0.0	ND

	PC				Si				PN		
	CBL	ODU	DHMH	DCLS	CBL	ODU	DHMH	DCLS	CBL	ODU	DCLS
3/7/94	1.7	6.8	ND	ND	1.2	0.6	3.5	3.1	1.5	3.4	ND
5/2/94	2.0	7.8	ND	ND	1.2	ND	22.2	0.0	2.2	10.0	ND
8/15/94	1.7	8.2	ND	ND	0.4	0.7	0.0	0.0	1.4	1.4	ND
11/14/94	5.1	2.0	ND	ND	0.0	0.9	0.0	0.0	4.3	12.4	ND
2/13/95	0.8	2.3	ND	ND	1.3	0.7	0.0	0.0	0.6	3.0	ND
5/8/95	0.9	5.2	ND	ND	4.7	4.8	0.0	24.7	1.8	0.6	ND
8/7/95	3.4	5.1	ND	ND	0.5	0.6	2.4	0.0	3.7	38.4	ND
11/13/95	4.2	10.5	ND	ND	2.0	1.8	3.2	0.0	3.1	12.1	ND
4/8/96	3.0	ND	0.1	28.0	1.0	0.8	2.7	0.0	1.3	ND	1.2
5/13/96	0.8	4.3	6.9	47.0	0.0	0.5	ND	0.0	4.5	37.3	7.5
8/5/96	1.4	0.5	4.2	53.7	0.0	3.3	0.0	0.0	1.2	2.5	4.4
11/20/96	6.3	ND	1.9	8.1	1.3	0.4	0.0	0.0	5.3	ND	1.5
3/4/97	3.8	12.9	0.3	30.6	0.0	0.5	6.7	0.0	4.2	18.8	0.7
6/9/97	0.0	2.3	1.9	36.8	2.5	2.9	4.0	0.0	1.3	3.3	1.9
9/8/97	0.9	5.4	3.6	25.5	1.3	0.4	1.2	0.0	0.3	3.9	4.0
12/8/97	0.9	6.2	4.8	64.4	34.6	14.8	ND	0.0	0.9	6.0	4.6
3/23/98	2.3	37.1	46.9	4.4	0.6	0.6	0.6	2.7	1.7	9.7	ND
6/11/98	0.9	13.4	30.6	ND	0.0	0.3	0.0	ND	0.7	2.8	ND
9/1/98	2.0	3.2	24.0	1.0	0.8	1.1	0.4	0.0	1.6	3.2	2.6
12/14/98	1.8	18.0	60.1	5.8	9.1	1.6	3.0	43.3	3.2	20.5	5.6

Appendix B

Blind Audit Report

Chesapeake Bay Program

Blind Audit Nutrient Results

January and June 1998

November 1998

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November 20, 1998

INTRODUCTION:

The purpose of this Blind Audit Program is to provide samples of specific nutrient analytes at concentrations commonly found in estuarine systems for analysis by laboratories who analyze water samples collected from the Chesapeake Bay and its tributaries. The concentrations of these samples, which are unknown to the recipient analysts, are compared to their true concentrations.

In the early years of the Chesapeake Bay Program, the U.S. EPA provided blind audit samples on an irregular basis to laboratories analyzing Chesapeake Bay water samples. However, these audit samples were designed for waste water/drinking water applications rather than estuarine water applications. Consequently, the concentrations were much higher than normally occur in the Bay and did not provide a reasonable estimate of accuracy for low level nutrient analyses. For example, a blind audit concentration of 1.0 mg NH4-N/L would be comparable for NPDES water samples but would be an order of magnitude greater than concentrations normally occurring in most parts of Chesapeake Bay.

The only continuous program providing an estimate of laboratory performance has been the Chesapeake Bay Coordinated Split Sample Program (CSSP). Data generated from this program provide the only long term QA/QC data base that compare nutrient measurements provided by laboratories analyzing water samples collected from Chesapeake Bay and its tributaries. Samples for the CSSP are natural water samples collected from Chesapeake Bay or a tributary. Briefly, a common unfiltered water sample is distributed to the various field/laboratory personnel who in turn subsample into dissolved and particulate fractions. These are analyzed and the results compared to those of other participating laboratories. Resulting data analysis can show how field filtration techniques and/or laboratory practices affect data variability. The CSSP samples are each subject to cumulative errors of analytical determinations from variation in both field and laboratory procedures. Also, these data sets cannot definitively determine the accuracy of laboratory analyses.

The current Blind Audit Program was designed to complement the CSSP. Blind Audit particulate samples distributed to participants have few cumulative errors associated with field filtering and subsampling procedures. Prepared concentrates of dissolved substances, whose concentrations are unknown to the analysts, are provided so that laboratory accuracy can be assessed.

There have been no blind audit assessments within the Chesapeake Bay Program for the past nine years. It is the intent of this Blind Audit Program to continually provide unknown, low level dissolved and particulate nutrient samples to laboratories analyzing Chesapeake Bay Program nutrients, as well as to other laboratories interested in participating in the Blind Audit Program.

MATERIALS AND METHODS

Blind Audit samples were sent to participating laboratories in January (27 January 1998) and June (15 June 1998) 1998. Those participating laboratories and contact personnel are found in Table 1.

Parameters measured during the January audit were: total dissolved nitrogen, total dissolved phosphorus, nitrate+nitrite, ammonium and phosphate. A high and a low concentration sample were provided for each of these analytes. Particulate carbon, nitrogen and phosphorus samples were also provided for those laboratories that routinely analyze these parameters.

Dissolved Blind Audit concentrates were prepared by careful dilution of high quality standards using 18.3 megohm deionized water. The concentrates were sealed in 10 mL ampules for shipment to the participants. One ampule contained a concentrate of an organic nitrogen compound and an organic phosphorus compound to be diluted for the analysis of low level total dissolved nitrogen and total dissolved phosphorus. A second ampule contained a concentrate of organic nitrogen and organic phosphorus to be diluted for the analysis of higher level total dissolved nitrogen and total dissolved phosphorus. A third ampule contained a concentrate to be diluted for the analysis of low level inorganic nutrients (ammonium, nitrate and phosphate). A fourth ampule contained a concentrate to be diluted for

the analysis of higher level inorganic nutrients. At each participating laboratory, an aliquot from each ampule was diluted and analyzed according to accompanying instructions for preparation and dilution. Blind Audit samples were then inserted randomly in a typical estuarine sample set. Final concentrations were reported for each diluted concentrate according to the dilution instructions provided.

Particulate analytes are measured by analyzing suspended material concentrated on filter pads. There are no commercially available suspensions of pure carbon, nitrogen or phosphorus compounds, so a natural sample was subsampled onto filter pads for analysis by participating laboratories. A batch water sample was collected off the CBL pier in January and June, and subsampled for particulate samples of carbon, nitrogen and phosphorus. Particulate C/N samples were filtered from the batch sample with care being taken to shake the sample before each filtration to ensure homogeneity. Four 25 mm GF/F pads were sent to each laboratory for analysis. One laboratory s instrument requires that only 13 mm filters be utilized. For that laboratory, four 13 mm GF/F pads were provided. Samples were dried completely (overnight at 47°C) before shipment. Vacuum filtration was used to process the 25 mm filters, but positive pressure was used to filter the 13 mm filters. Our laboratory did not have the facilities necessary to vacuum filter these small filters.

The same general procedure was followed for particulate phosphorus samples which were concentrated by vacuum filtration on 47 mm GF/F pads.

Particulate concentrations for the January Blind Audit were estimated as closely as possible by analyzing at least eight replicates of each analyte by Chesapeake Biological Laboratory. These calibration replicates also provided an estimate of variability due to the cumulative effect of filtering and other processing errors. Filter pads were sent to each laboratory for the analysis of particulate C, N and P. The volume of sample filtered was noted in the instructions so that each laboratory could report values in mg/L.

For the June Blind Audit, two samples concentrated on filters were supplied to each laboratory for each particulate analysis. One laboratory analyzed a second pair of filters because the first pair was rejected when the analyst noticed a marked visible difference between the replicates. The standard deviations determined for the January particulate fractions also were used to assess the variability of the June data.

Analysis of chlorophyll *a* samples was added to the suite of nutrients in June 1998. Samples were filtered onto 47 mm GF/F glass fiber filters and two were then sent to each laboratory.

For both audits, samples were sent in coolers via next day carrier to the participating laboratories. In June, when chlorophyll samples were sent, a cold temperature was required, so frozen cold packs were packed in those coolers.

RESULTS

JANUARY 1998 DISSOLVED FRACTION

Figures summarizing all results are found at the end of the report.

Total Dissolved Nitrogen: The true low level concentration was 0.35 mg N/L and reported concentrations ranged from 0.27-0.40 mg N/L. The true high level concentration was 1.05 mg N/L and reported concentrations ranged from 0.97-1.15 mg N/L. All laboratories reported concentrations that were within 0.10 mg N/L of the respective total dissolved nitrogen concentrations.
Total Dissolved Phosphorus: The true low level concentration was 0.024 mg P/L and reported concentrations ranged from 0.020-0.040 mg P/L. The true high level concentration was 0.096 mg P/L and reported concentrations ranged from 0.050-0.110 mg P/L.. All laboratories except one reported concentrations within 0.005 mg P/L of the true concentration for the low level total dissolved phosphorus sample. All laboratories except one reported concentrations within 0.015 mg P/L of the true concentration

for the higher level total dissolved phosphorus concentration.

Ammonium: The true low level concentration was 0.063 mg N/L and reported concentrations ranged from 0.060-0.081 mg N/L. The true high level concentration was 0.330 mg N/L and reported concentrations ranged from 0.320-0.364 mg N/L. All laboratories except one reported concentrations within 0.006 mg N/L of the true low level ammonium concentration. All laboratories reported concentrations within 0.034 mg N/L of the true higher level ammonium concentration.

Nitrate+nitrite: The true low level concentration was 0.112 mg N/L and reported concentrations ranged from 0.110-0.126 mg N/L. The true high level concentration was 1.15 mg N/L and reported concentrations ranged from 1.12-1.23 mg N/L.. All laboratories reported concentrations within 0.014 mg N/L of the true low level nitrate concentration, and within 0.08 of the true higher level nitrate concentration.

Phosphate: The true low level concentration was 0.031 mg P/L and reported concentrations ranged from 0.020-0.040 mg P/L. The true high level concentration was 0.310 mg P/L and reported concentrations ranged from 0.298-0.335 mg P/L. All laboratories except two reported concentrations within 0.003 mg P/L of the true low level phosphate concentration. All laboratories reported concentrations within 0.025 mg P/L of the true higher level phosphate concentration.

JANUARY 1998 PARTICULATE FRACTION

Again, it should be noted that these samples were filtered from a common water sample and, consequently, are not true blind audit samples made from pure constituents; rather, a concentration range around a mean was established by the analysis of 12 replicate particulate C/N samples and 8 replicate particulate phosphorus samples. This still provides a verification of measurement processes in routine analytical conditions at participating laboratories, without the potential variability associated with differing field filtration techniques.

Particulate Nitrogen: The mean concentration of the 12 replicate samples was 0.078 mg N/L ± 0.004 (S.D.) and all but one of the responding laboratories reported the mean concentration of their four replicates within 0.078 mg N/L ± 0.012, i.e., 3 X S.D. .

Particulate Carbon: The mean concentration of the 12 replicate samples was 0.411 mg C/L ± 0.050 (S.D.) and all responding laboratories reported the mean concentration of their four replicates within 0.411 mg C/L ± 0.150, i.e., 3 X S.D..

Particulate Phosphorus: The mean concentration of the 8 replicate samples was 0.0318 mg P/L ± 0.0010 (S.D.) and all responding laboratories reported the mean concentration of their four replicates within 0.0318 mg P/L ± 0.0030, i.e., 3 X S.D..

JUNE 1998 DISSOLVED FRACTION

The concentrations of some Blind Audit samples were reduced for the June audit. Low level total dissolved N and P concentrations remained unchanged from the January concentrations, but the higher level concentrations were halved from those of January. Low level ammonium concentrations were also halved, as were the low level phosphate concentrations. The higher level concentration phosphate samples were reduced by a factor of five from the June samples. Basically, for the June Blind Audit, the true concentrations remained unchanged or were substantially reduced from January levels.

Total Dissolved Nitrogen: The true low level concentration was the same as in January, 0.35 mg N/L and reported concentrations ranged from 0.205-0.42 mg N/L. The true high level concentration was 0.53 mg N/L and reported concentrations ranged from 0.39-0.62 mg N/L. All laboratories reported concentrations

within 0.15 mg N/L of the true concentration of the respective total dissolved nitrogen concentrations.

Total Dissolved Phosphorus: The true low level concentration was 0.024 mg P/L (the same as January) and reported concentrations ranged from 0.020-0.030 mg P/L. The true high level concentration was 0.048 mg P/L and reported concentrations ranged from 0.030-0.0513 mg P/L. All laboratories reported concentrations within 0.006 mg P/L of the true low level total dissolved phosphorus concentration. All laboratories except one reported concentrations within 0.006 mg P/L of the true higher level total dissolved phosphorus concentration.

Ammonium: The true low level concentration was 0.035 mg N/L and reported concentrations ranged from 0.025-0.040 mg N/L. The true high level concentration was 0.280 mg N/L and reported concentrations ranged from 0.2645-0.281 mg N/L. All laboratories reported concentrations within 0.010 mg N/L of the true low level ammonium concentration, and within 0.020 of the true higher level ammonium concentration.

Nitrate+nitrite: The true low level concentration was 0.175 mg N/L and reported concentrations ranged from 0.160-0.210 mg N/L. The true high level concentration was 0.600 mg N/L and reported concentrations ranged from 0.550-0.594 mg N/L. All laboratories except one reported concentrations within 0.015 mg N/L of the true low level nitrate concentration. All laboratories reported concentrations within 0.050 mg N/L of the true higher level nitrate concentration.

Phosphate: The true low level concentration was 0.0186 mg P/L and reported concentrations ranged from 0.0190-0.0203 mg P/L. The true high level concentration was 0.0620 mg P/L and reported concentrations ranged from 0.0600-0.0672 mg P/L. All laboratories reported concentrations within 0.0020 mg P/L of the true low level phosphate concentration, and within 0.0060 of the true higher level phosphate concentration.

JUNE 1998 PARTICULATE FRACTION

Particulate Nitrogen: The mean concentration of the samples analyzed by the five participating laboratories was 0.307 mg N/L. Each reported mean from any participating laboratory was within 0.307 mg N/L $\pm$ 0.012, i.e., 3 X S.D. of the 12 January calibration replicates.

Particulate Carbon: The mean concentration of the samples analyzed by the five participating laboratories was 1.60 mg C/L. Each reported mean from any participating laboratory was within 1.60 mg C/L $\pm$ 0.15, i.e., 3 X S.D. of the 12 January calibration replicates.

Particulate Phosphorus: The mean concentration of the samples analyzed by the five participating laboratories was 0.0454 mg P/L.. Each reported mean from any participating laboratory was within 0.0454 mg P/L $\pm$ 0.0030, i.e., 3 X S.D. of the 8 January calibration replicates.

Chlorophyll: There was quite large variation between laboratories in the chlorophyll *a* concentrations reported. CBL and DCLS reported nearly identical concentrations, while the Academy of Natural Sciences was more than 7 μg/L greater, and VIMS and ODU reported concentrations substantially lower.

DISCUSSION

Three important issues should be considered when assessing whether individual Blind Audit results are within acceptable limits.

Variation Associated With An Analytical Method: A certain amount of analytical variability is associated with any quantitative determination. The method detection limit (three times the standard deviation of seven low level replicate natural samples) is often used to express that level of variation. Total dissolved

nitrogen data provide a good example. The detection limit at CBL has been determined to be 0.02 mg N/L. Any total dissolved nitrogen measurement has a potential 0.02 mg N/L variability associated with it. This variability, when expressed as a percent of the true concentration, can be extremely large for low level concentrations and fairly low for higher concentrations. For example, a 0.20 mg N/L concentration has an analytical variability of 10% associated with it; whereas, a 1.20 mg N/L concentration has an analytical variability of 2%.

Reporting Significant Figures: The number of significant figures used by a laboratory to report analytical results can significantly affect data interpretation in a blind audit study. If a laboratory reports only two significant figures (for whatever reasons) and an audit sample has a true concentration expressed in three significant figures, then substantial under or over estimates of the true concentration can be reported. For example, if a true value of 0.035 mg P/L has been prepared and a laboratory only reports two significant figures, i.e., 0.03 mg P/L, then the results expressed are 86% of the expected true value.

Preparation of True Standards: Companies that prepare large quantities of unknowns assign acceptable confidence limits around the true value. In one case (SPEX, CertiPrep), the mean recovery and standard deviation are later reported along with the true concentration and the 95% confidence interval (CI). The 95% CI represents the mean recovery $\pm$ 2 standard deviations and was developed from regression equations from Water Pollution Performance Evaluation Studies. A recently purchased set of these standards gave a true total P value of 3.00 mg P/L with a 95% CI of 2.47-3.42 mg P/L.. The lower end of the 95% CI recovery allows 82% recovery of the true concentration. This type of statistical analysis was not performed on the Blind Audit Program samples prepared for this study.

With the above issues in mind and even though only two rounds of the Blind Audit Program have been completed, some consistent patterns have been observed that warrant discussion or further investigation:

1. Reported concentrations of all analytes except total dissolved phosphorus and chlorophyll *a* are similar between laboratories participating in the Blind Audit Program. Except for total dissolved phosphorus, no laboratory reported concentrations for an individual analyte that were consistently different from the range of the other reported concentrations. This probably indicates that all participating laboratories execute these measurements with accuracy and precision.

2. If possible, all participants should report data from future Blind Audits to three significant figures to facilitate concentration comparisons.

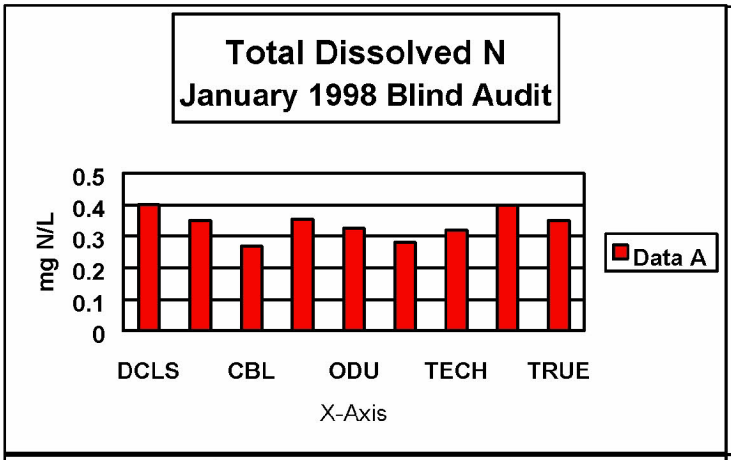
3. A 95% Confidence Interval for each concentration level of every analyte should be established, possibly with the assistance of EPA statisticians.

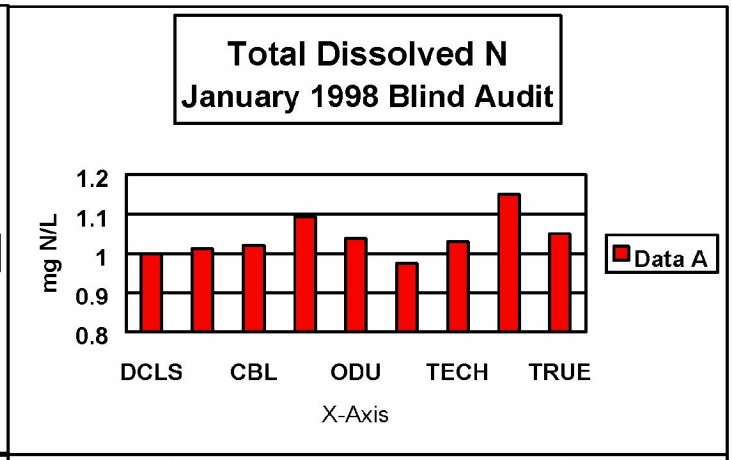
4. One laboratory reported consistently lower concentrations for total dissolved phosphorus in both the low and higher level samples. Although other laboratories reported concentrations for the low level sample that were similar, none reported similar concentrations for the higher level samples.

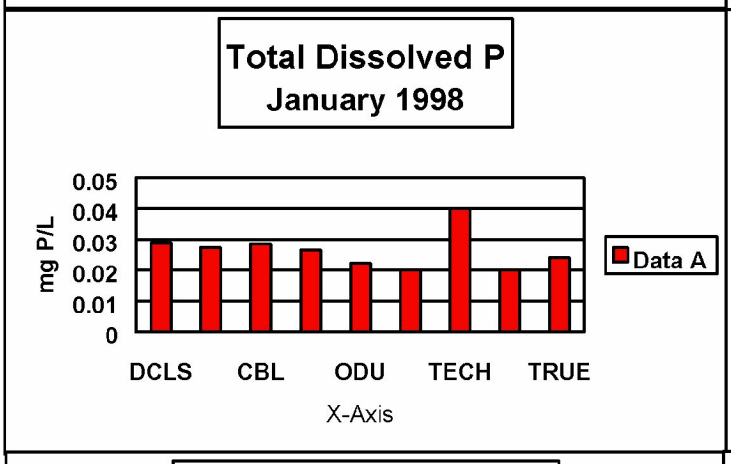
5. Reported chlorophyll *a* concentrations were quite variable. In connection with these data and other CBP chlorophyll *a* data anomalies, the CBP Quality Assurance Officer is contacting all participants with respect to methodology--spectrophotometric-one wave length/trichromatic/fluorometric; type of grinding; use of buffers; etc.

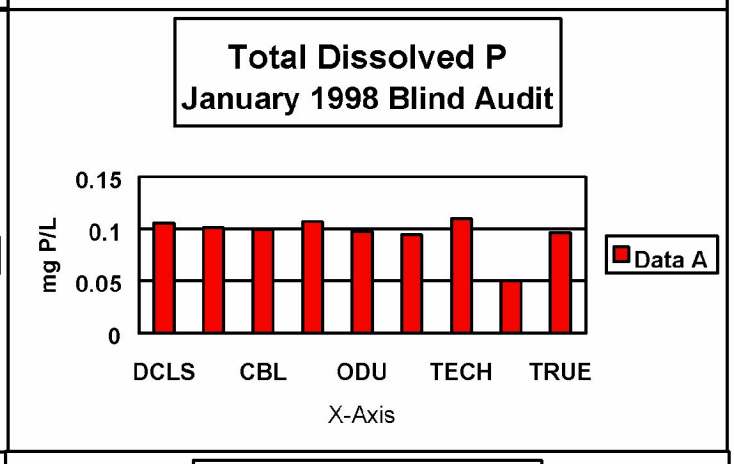
Table 2 lists concentrations of analytes where the difference between the reported concentration and the true concentration was more than two times a typical MDL in both the January and June Blind Audits. These differences may not be cause for concern since 95% confidence intervals have not been assigned.

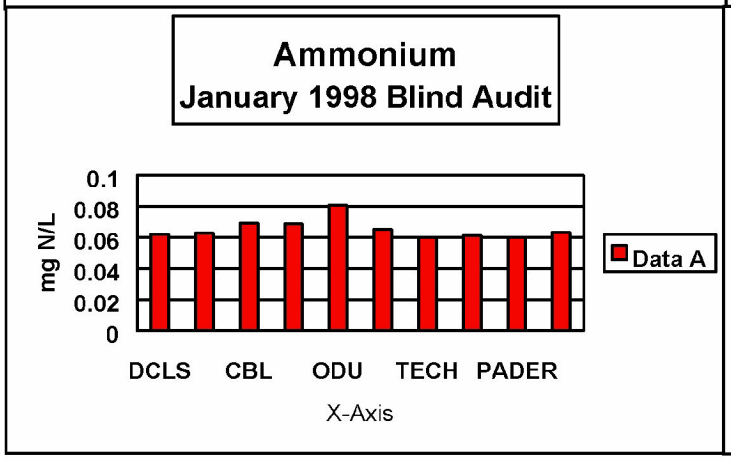
Table 2. Consistent differences noted in 1998 Blind Audit results							
Total Dissolved Nitrogen; Low Concentration (mg N/L)							
January					June		
Lab.	True	Reported	% of True		True	Reported	% of True
CBL	0.35	0.27	77%		0.35	0.30	86%
HPL	0.35	0.281	80%		0.35	0.205	59%
PADER	0.35	0.40	114%		0.35	0.42	120%
Total Dissolved Nitrogen; High Concentration (mg N/L)							
January					June		
Lab.	True	Reported	% of True		True	Reported	% of True
PADER	1.05	1.15	109%		.53	.62	117%
Total Dissolved Phosphorus; Low Concentration (mg P/L)							
January					June		
Lab.	True	Reported	% of True		True	Reported	% of True
CBL	.024	.0285	119%		.024	.0205	85%
HPL	.024	.020	83%		.024	.021	87%
PADER	.024	.02	83%		.024	.02	83%
Total Dissolved Phosphorus, High Concentration (mg P/L)							
January					June		
Lab.	True	Reported	% of True		True	Reported	% of True
PADER	.096	.05	52%		.048	.03	62%

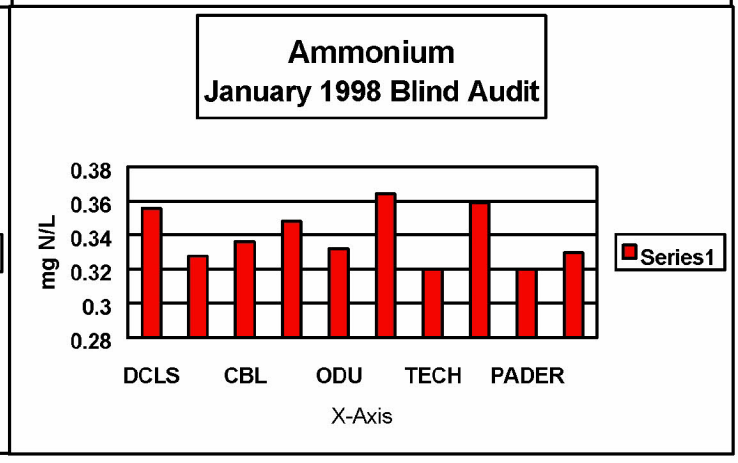

Total Dissolved N
January 1998 Blind Audit
mg N/L
0.5
0.4
0.3
0.2
0.1
0
DCLS
CBL
ODU
TECH
TRUE
X-Axis
Data A

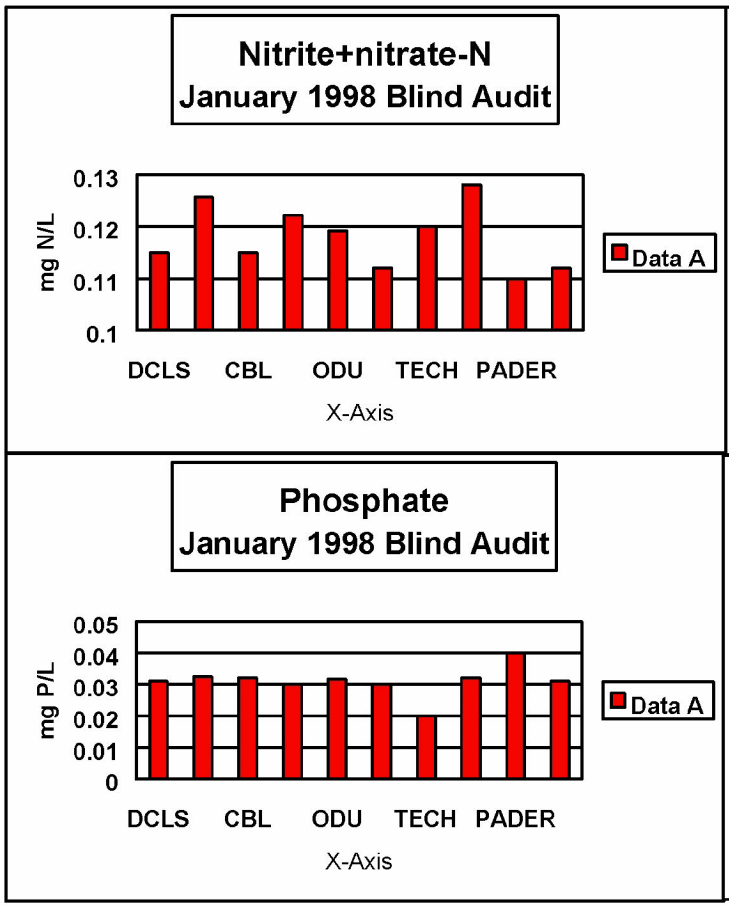

Total Dissolved N
January 1998 Blind Audit
mg N/L
1.2
1.1
1
0.9
0.8
DCLS
CBL
ODU
TECH
TRUE
X-Axis
Data A

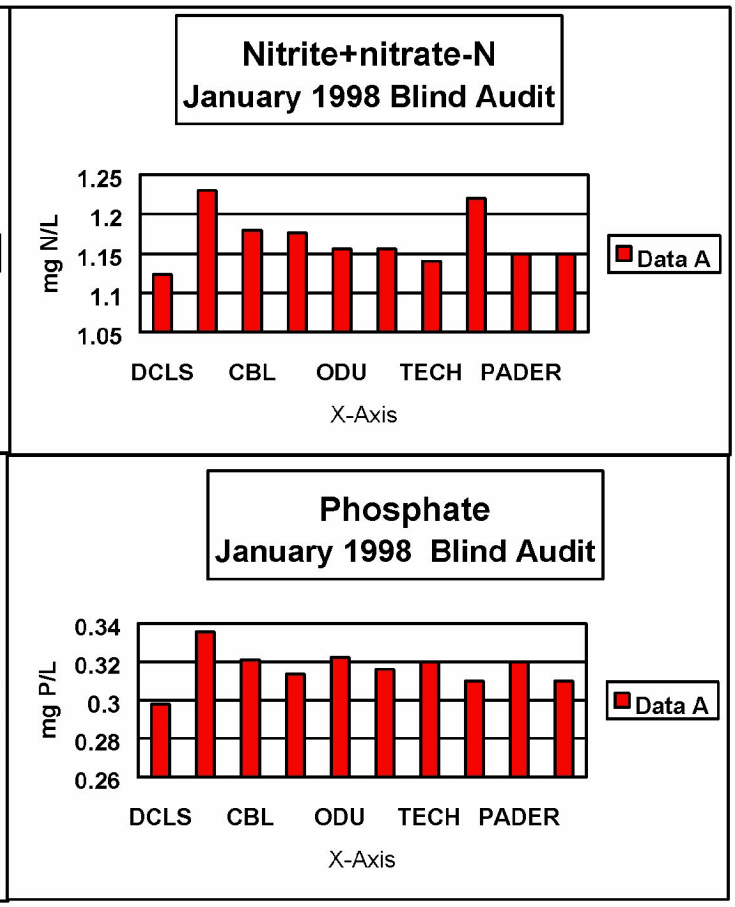

Total Dissolved P
January 1998
mg P/L
0.05
0.04
0.03
0.02
0.01
0
DCLS
CBL
ODU
TECH
TRUE
X-Axis
Data A


Total Dissolved P
January 1998 Blind Audit
mg P/L
0.15
0.1
0.05
0
DCLS
CBL
ODU
TECH
TRUE
X-Axis
Data A


Ammonium
January 1998 Blind Audit
mg N/L
0.1
0.08
0.06
0.04
0.02
0
DCLS
CBL
ODU
TECH
PADER
X-Axis
Data A

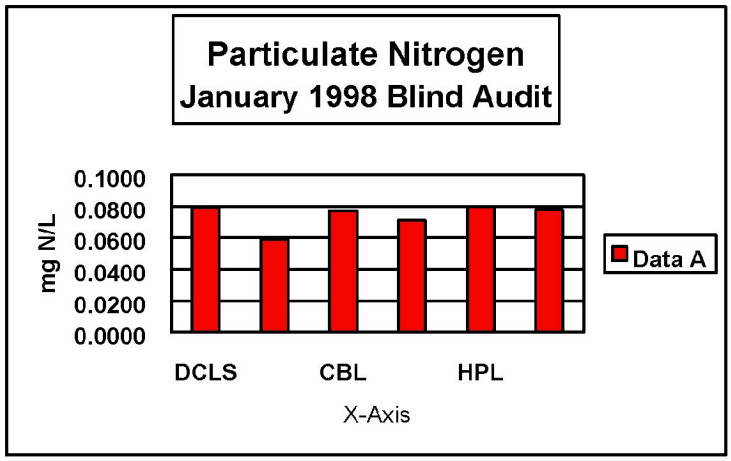

Ammonium
January 1998 Blind Audit
mg N/L
0.38
0.36
0.34
0.32
0.3
0.28
DCLS
CBL
ODU
TECH
PADER
X-Axis
Series1

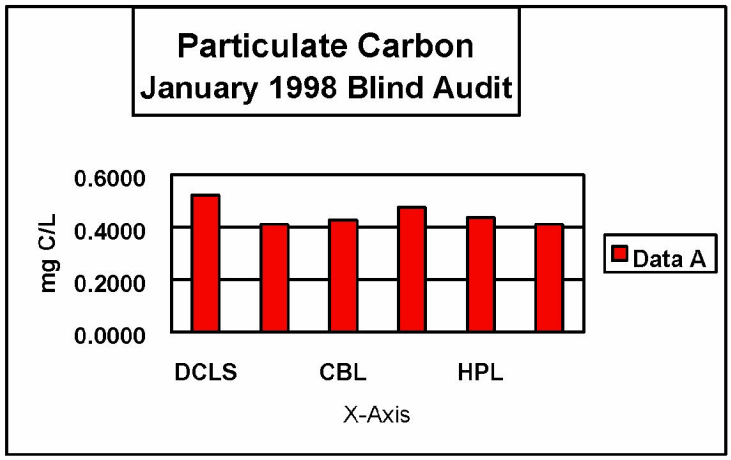

Nitrite+nitrate-N
January 1998 Blind Audit
mg N/L
0.13
0.12
0.11
0.1
DCLS
CBL
ODU
TECH
PADER
X-Axis
Data A

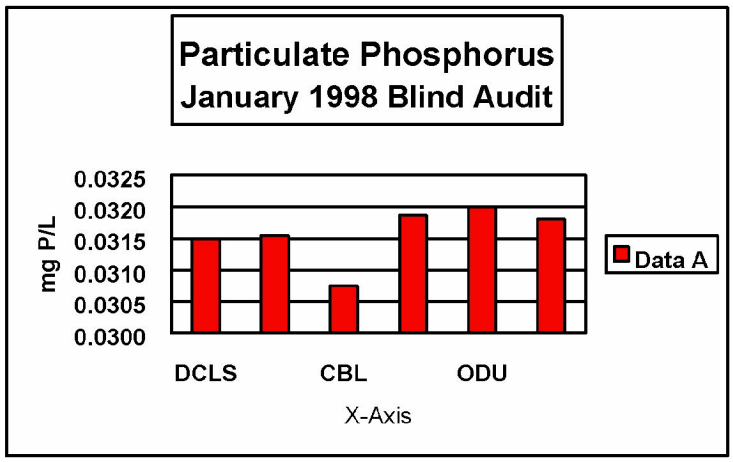

Nitrite+nitrate-N
January 1998 Blind Audit
mg N/L
1.25
1.2
1.15
1.1
1.05
DCLS
CBL
ODU
TECH
PADER
X-Axis
Data A

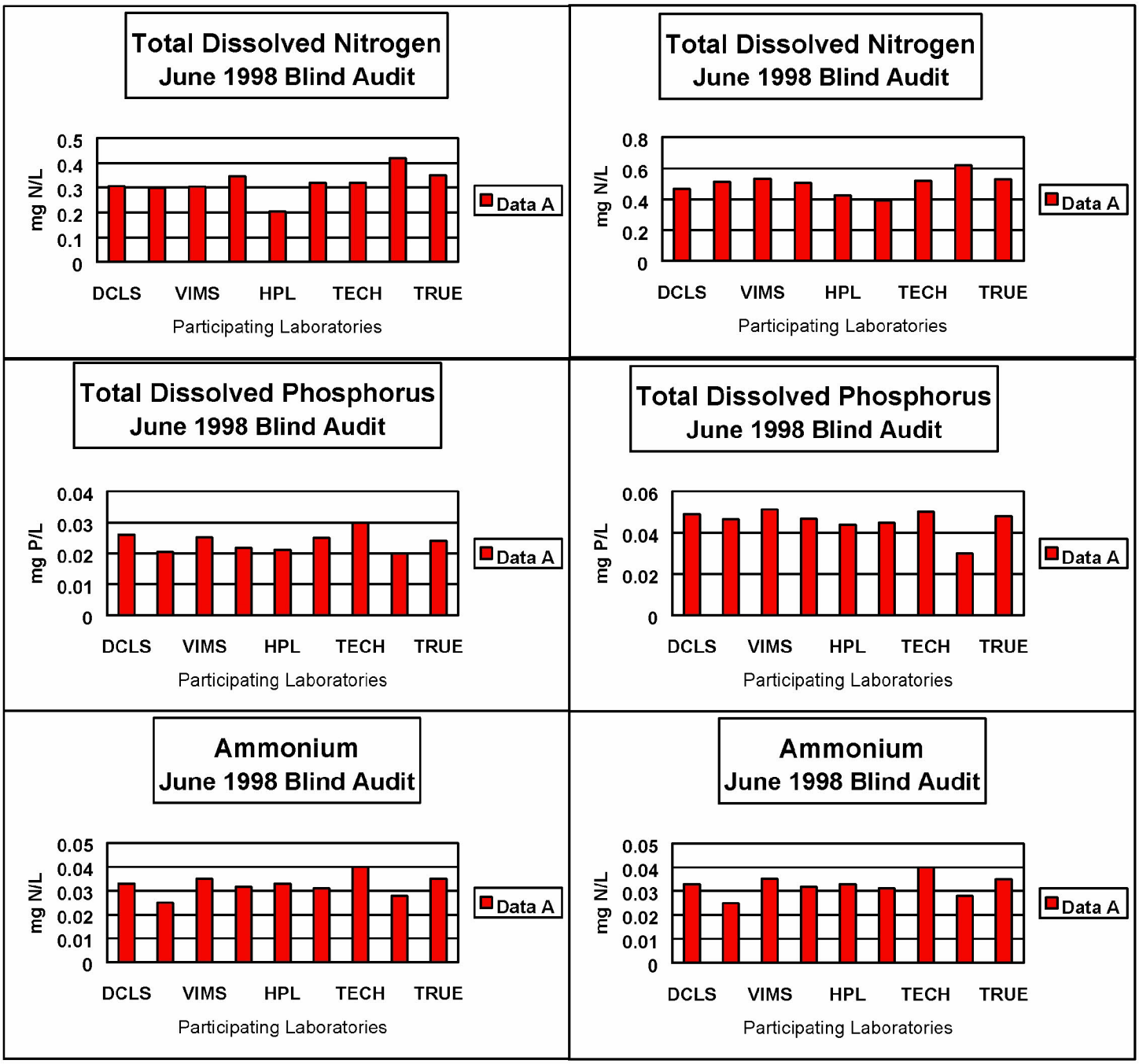
Phosphate
January 1998 Blind Audit
mg P/L
0.05
0.04
0.03
0.02
0.01
0
DCLS
CBL
ODU
TECH
PADER
X-Axis
Data A

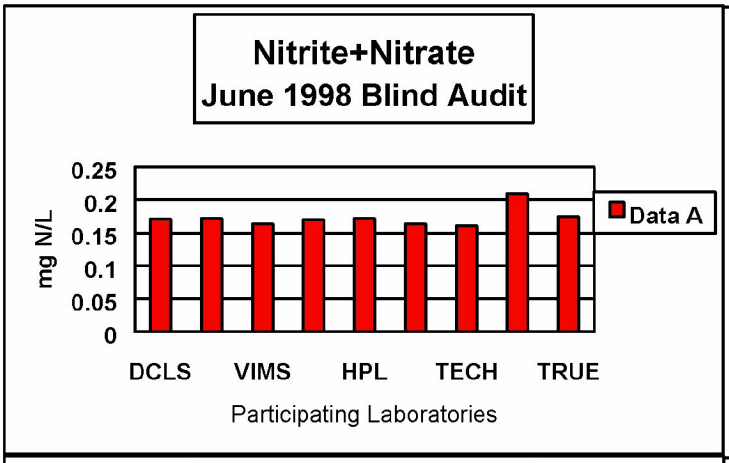
Phosphate
January 1998 Blind Audit
mg P/L
0.34
0.32
0.3
0.28
0.26
DCLS
CBL
ODU
TECH
PADER
X-Axis
Data A

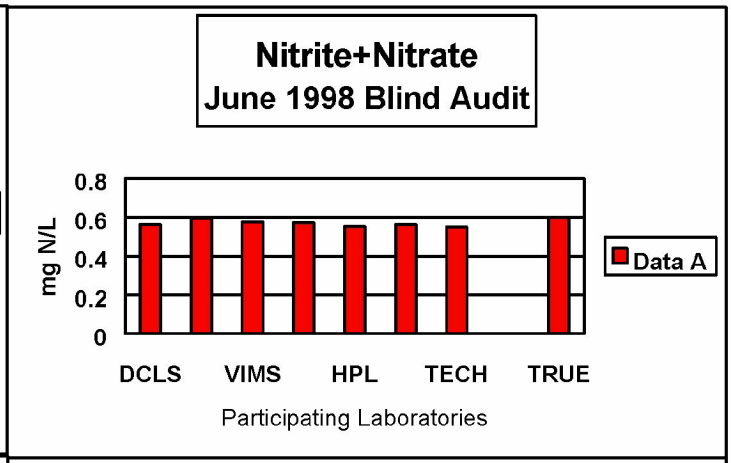

Particulate Nitrogen
January 1998 Blind Audit
mg N/L
0.1000
0.0800
0.0600
0.0400
0.0200
0.0000
DCLS
CBL
HPL
X-Axis
Data A

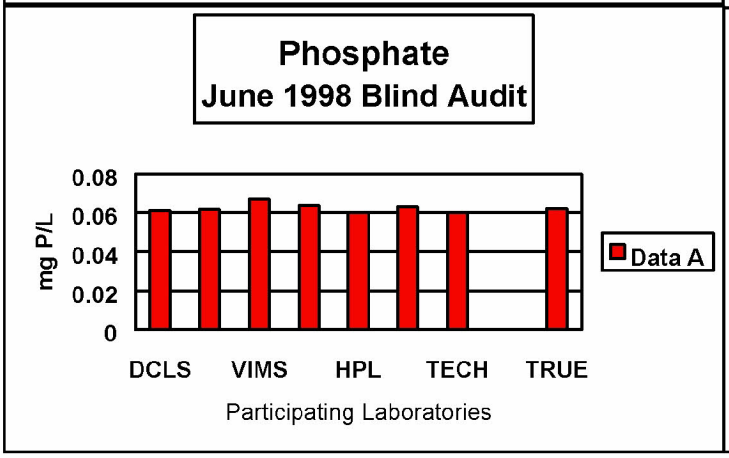

Particulate Carbon
January 1998 Blind Audit
mg C/L
0.6000
0.4000
0.2000
0.0000
DCLS
CBL
HPL
X-Axis
Data A


Particulate Phosphorus
January 1998 Blind Audit
mg P/L
0.0325
0.0320
0.0315
0.0310
0.0305
0.0300
DCLS
CBL
ODU
X-Axis
Data A


Total Dissolved Nitrogen
June 1998 Blind Audit
mg N/L
0.5
0.4
0.3
0.2
0.1
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A
Total Dissolved Nitrogen
June 1998 Blind Audit
mg N/L
0.8
0.6
0.4
0.2
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A
Total Dissolved Phosphorus
June 1998 Blind Audit
mg P/L
0.04
0.03
0.02
0.01
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A
Total Dissolved Phosphorus
June 1998 Blind Audit
mg P/L
0.06
0.04
0.02
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A
Ammonium
June 1998 Blind Audit
mg N/L
0.05
0.04
0.03
0.02
0.01
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A
Ammonium
June 1998 Blind Audit
mg N/L
0.05
0.04
0.03
0.02
0.01
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A


Nitrite+Nitrate
June 1998 Blind Audit
mg N/L
0.25
0.2
0.15
0.1
0.05
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A


Nitrite+Nitrate
June 1998 Blind Audit
mg N/L
0.8
0.6
0.4
0.2
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A


Phosphate
June 1998 Blind Audit
mg P/L
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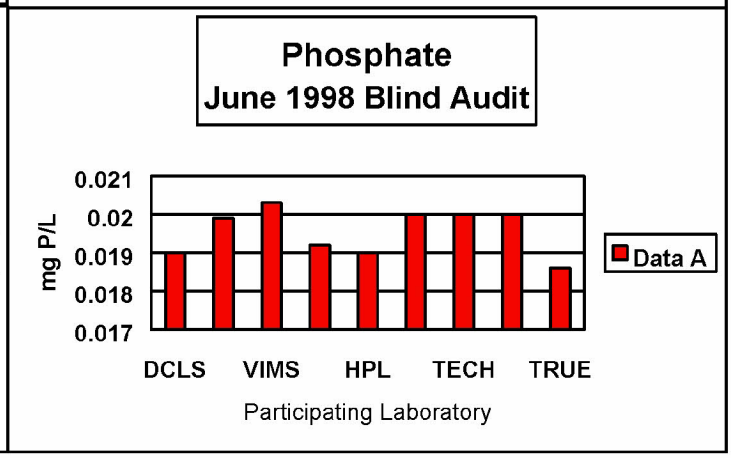
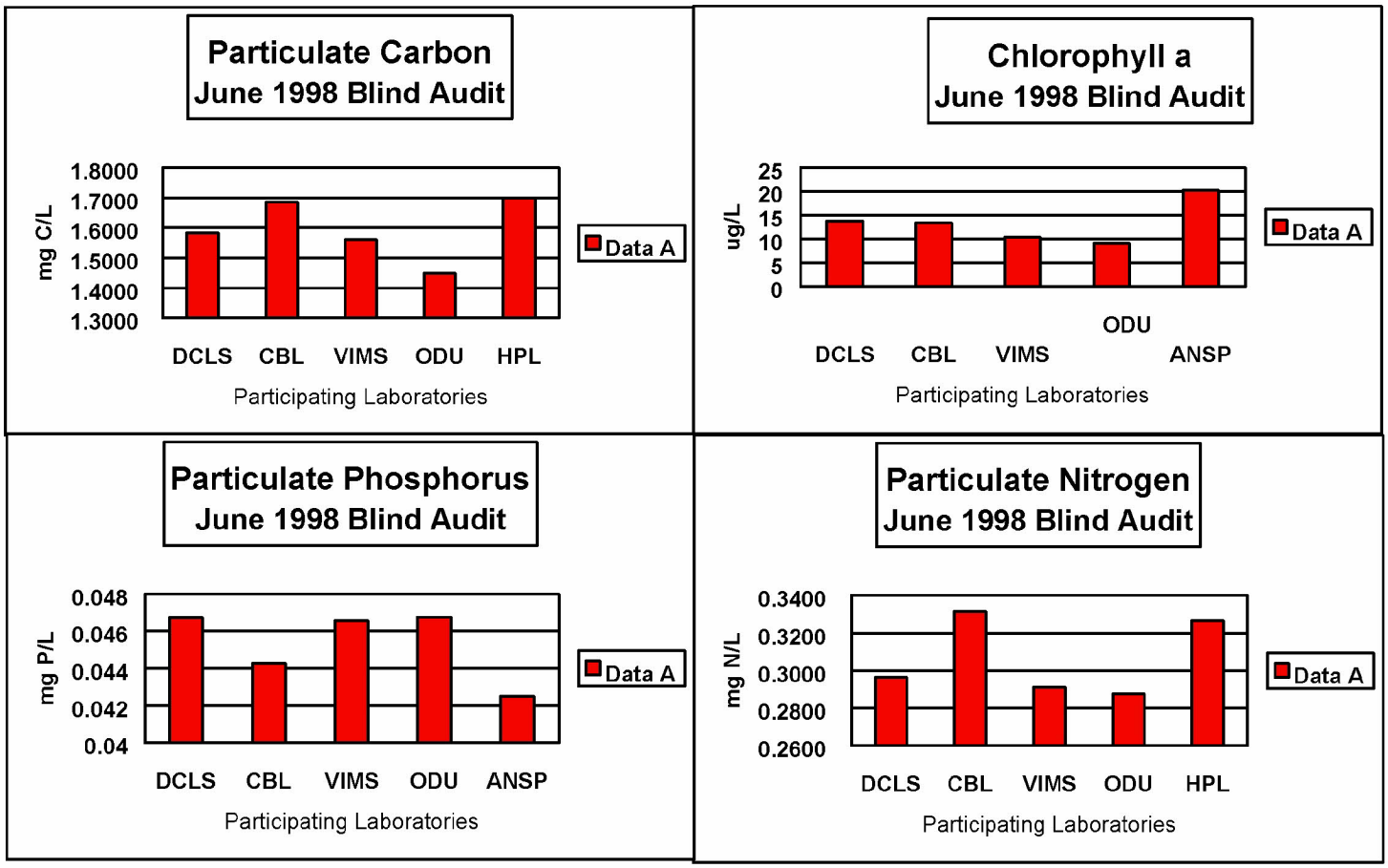
0.06
0.04
0.02
0
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratories
Data A


Phosphate
June 1998 Blind Audit
mg P/L
0.021
0.02
0.019
0.018
0.017
DCLS
VIMS
HPL
TECH
TRUE
Participating Laboratory
Data A


Particulate Carbon
June 1998 Blind Audit
mg C/L
1.8000
1.7000
1.6000
1.5000
1.4000
1.3000
DCLS CBL VIMS ODU HPL
Participating Laboratories
Data A
Chlorophyll a
June 1998 Blind Audit
ug/L
25
20
15
10
5
0
DCLS CBL VIMS ODU ANSP
Participating Laboratories
Data A
Particulate Phosphorus
June 1998 Blind Audit
mg P/L
0.048
0.046
0.044
0.042
0.04
DCLS CBL VIMS ODU ANSP
Participating Laboratories
Data A
Particulate Nitrogen
June 1998 Blind Audit
mg N/L
0.3400
0.3200
0.3000
0.2800
0.2600
DCLS CBL VIMS ODU HPL
Participating Laboratories
Data A